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H. P. TALBOT, PH. D., CONSULTING EDITOR

THE SAMPLING AND CHEMICAL ANALYSIS OF IRON AND STEEL

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THE SAMPLING AND CHEMICAL ANALYSIS OF IRON AND STEEL

BY

O. BAUER AND E. DEISS

OF THE

ROYAL TESTING BUREAU AT GROSS-LICHTERFELDE, GERMANY

AUTHORIZED
TRANSLATION FROM THE GERMAN

BY

WILLIAM T. HALL AND ROBERT S. WILLIAMS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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PREFACE

During many years of service in the Royal Testing Bureau the authors have noticed again and again how carelessly and often quite unscientifically the sampling of iron and steel for chemical analysis is carried out.

The practical man usually assumes that the material for analysis has the same composition throughout its entire cross-section and that it is immaterial, therefore, where and how the samples are taken. This assumption is often incorrect.

The complaints made against chemists, in cases of bad agreement in analytical results, are often unjust because the differences in chemical composition due to segregation are frequently much greater than the possible errors in the analytical procedures.

Fortunately, however, with the aid of metallography and the macroscopic study of the structure, the chemist is now able to determine quickly and with certainty whether segregation has taken place.

The first part of this book shows, by means of numerous examples taken from metallographic practice, how seriously the analytical results can be influenced by incorrect sampling. Before discussing them, a brief introduction to Metallography is given with a description of the necessary apparatus, the methods of etching, and the characteristic appearance of the different constituents.

In the second part, the methods of chemical analysis are given in detail. In collecting these methods the main object has been to include only those methods which have been found reliable and have undergone the test of a number of years' use at the Royal Testing Bureau. They are suitable, therefore, for test and umpire analyses. Descriptions of the very rapid "works methods" are omitted because these processes aim to give quick results rather than values of great accuracy.

The authors wish to express their obligations to Professor A. Martens, Director of the Bureau, and to Associate Director, Professor E. Heyn, for permission to use the entire equipment of the laboratory in the preparation of the book. The microphotographs, for example, are all taken from the Bureau's collection of over 6000 plates.

O. Bauer,
E. Deiss.

TRANSLATORS' PREFACE

The first part of the book, concerning the proper sampling of iron and steel, was written by Professor Bauer and has been translated with very few changes in the text. The translators have felt for a long time that too little attention has been paid by American chemists to the effects of segregation and this is one of the chief reasons for translating the book.

The second part of the book which includes tested methods for the chemical analysis of iron and steel was written by E. Deiss. This part of the book has been amplified by the translators to a considerable extent. The attempt has not been made, as in some other texts, to include all the best-known methods but rather to give only those which are reasonably sure to give accurate results in the hands of even a relatively inexperienced chemist. The work done by a number of chemists in connection with the establishment of Standard Samples of Iron and Steel by the Bureau of Standards at Washington, D. C., has shown beyond any doubt that many of the rapid methods give results which are nearly, if not quite, as good as those obtained by much more laborious procedures. In the busy analytical laboratory time is such an important factor that it must always be taken into consideration. The translators, therefore, have included about twenty-five methods which are not given in the German edition. These methods have, for the most part, been thoroughly tested in the laboratories at the Massachusetts Institute of Technology.

Among the methods added, is that of Walker and Patrick for the determination of combined oxygen. This is a method which requires considerable skill to carry out successfully. It is included in spite of this, because it is probably the best method that has been devised for determining all the oxygen that may be present in a sample of iron and steel.

WILLIAM T. HALL,
ROBERT S. WILLIAMS.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
July, 1915.

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PART I

THE SAMPLING OF IRON AND STEEL

BY

O. BAUER

TRANSLATED BY

ROBERT S. WILLIAMS

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SECTION II

SPECIAL CASES. CONDITIONS WHICH MAKE THE TAKING OF REPRESENTATIVE SAMPLES DIFFICULT

SECTION I

GENERAL DISCUSSION OF SAMPLING AND THE MEANS OF OBTAINING REPRESENTATIVE SAMPLES

CHAPTER I

THE IMPORTANCE OF PROPER SAMPLING FOR CHEMICAL ANALYSES

The sampling of large quantities of raw materials used in the iron and steel industry, *e.g.*, car loads of pig iron, ship loads of iron ores, of manganese ores, of coke, etc., has already been discussed in numerous published papers[1] and in technical treatises.[2] The importance of proper sampling for judging and evaluating such materials, both from the standpoint of the buyer and of the seller, has been pointed out. In large plants, either the chief chemist himself or a properly trained assistant is personally responsible in this matter and it is quite right that it should be so. The sampling of the raw materials, therefore, will not be considered in this book.

The sampling of intermediate products (pigs, ingots, bars, etc.) and of manufactured articles (castings, rolled iron, shaped iron, plates, etc.) for the purpose of chemical analysis has, for the most part, been discussed very superficially in the literature. The value of proper sampling in technical work is not properly recognized or appreciated. Quite often in practice the chemist in charge, who is responsible for the accuracy of the results, has nothing whatever to say about the way in which samples submitted to him for analysis shall be taken. He can, indeed,

[1] *cf.* C. Bender, Stahl u. Eisen, **1903,** 309; W. J. Rattle and Son, Eng. and Min. J., **80,** 824 (1905). See also "Methods of Sampling and Analysis used by the U. S. Steel Cor.," Stahl u. Eisen, **1910,** 556.

[2] *cf.* The manuals for metallurgical laboratories by Ledebur, Wedding and others.

assume the responsibility for correct chemical analyses, but cannot guarantee that the values given for the different constituents (phosphorus, sulfur, carbon, etc.) actually represent the average composition of the sample, since *the composition of the sample is not necessarily uniform throughout its entire cross-section but is often quite the reverse.*

For this reason, judgment based on the chemical analysis alone is not always correct as the analytical results are influenced to a marked degree by the methods of sampling. Control analyses made by different chemists on borings from the same piece, are of value only when the sample to be analyzed is known to be uniform throughout its whole cross-section. Much of the disagreement among chemists as to the methods to be used is probably due to lack of uniformity in the samples analyzed and to improper sampling.

H. E. Field[1] has mentioned the value of chemical analysis as a means of classifying pig iron and stated that "The one great argument against the use of chemistry for the grading of iron has been that the work of chemists varied so much that it was impossible to obtain anything like uniform results."

That the chemist is responsible for these conditions only to a very limited extent will be shown in this book. Irregularities in the chemical composition of the sample due to local segregation are often far greater than the possible errors of analysis. This is true not only of pig iron but also of all other kinds of iron and steel.

Metallography is of the utmost value to the chemist in helping him to detect such local differences. In many cases it is impossible to determine whether local differences in chemical composition really exist in any other way than by metallographic study.

It is for this reason not only to the interest of the employer but also to the chemist's own advantage that the following conditions be fulfilled:

1. The chief chemist should be trained in metallography.

2. A metallographic laboratory, even though a small one, should be connected with every steel-works laboratory.

[1] Iron Trade Review, Feb. 26, 1903.

3. In all cases the taking of samples should be directly in charge of the one responsible for the subsequent analysis.[1]

The control of the sampling should cover not only the places at which samples are to be taken but also the way they should be taken, whether by boring, by filing, or by planing, and the way the samples should be handled; failure at any stage to observe proper precautions is likely to have an influence upon the final results, as will be shown in the following chapters.

Wherever metallographic laboratories are already established, as in many of the larger plants, it is highly desirable that they should be kept in intimate touch with the chemical laboratory.

An essential advantage which metallographic study has over ordinary chemical analysis is that it shows the structure of the material, the distribution of foreign matter in it, besides frequently indicating the nature of improper treatment in the case of imperfect material; while chemical analysis gives merely the percentage composition of the parts tested.[2]

[1] An exception is, of course, made with regard to the taking of samples during the actual smelting for the control of the furnaces.

[2] *cf.* E. Heyn, Diseased Conditions in Iron and Copper, Z. Ver. deutsch. Ing., **1902.** Henry Fay, Some Causes of Failure in Metals, Proc. Am. Soc. Test. Mat., **11,** 439 (1911).

CHAPTER II

ARRANGEMENT OF A METALLOGRAPHIC LABORATORY TO BE USED AS AN AID IN TAKING SAMPLES FOR ANALYSIS

The following outfit is suggested for use in connection with a chemical laboratory. Its chief purpose is to help the chemist to get satisfactory samples of iron and steel for analysis and to make it possible for him to recognize irregularities in the composition of specimens, so far as the present status of the metallography of iron makes that possible and in this way to avoid serious errors in sampling. For this reason only the apparatus absolutely necessary for the purpose will be described, with the most important etching mediums and their uses. A brief description of the metallographic characteristics of the common constituents and some of the impurities of iron and steel will be given.[1] A general knowledge of metallography (*e.g.*, familiarity with the Iron-Carbon Equilibrium Diagram) is assumed.

1. Hints on Taking Samples.—In taking samples for metallographic study the following fundamental rule always holds: Whenever possible examine a piece of the metal which will show either the entire cross-section or the longitudinal section of the specimen to be examined. Cutting a small piece out of a large area is worse than useless as the purpose of the metallographic study is to determine whether the specimen to be analyzed is homogeneous throughout.

The cutting out and planing of the test specimen is carried out as a rule in the machine shop, but it should always be done under

[1] For the outfit of larger metallographic laboratories such as are necessary for more elaborate investigations, the reader is referred to a paper by A. Martens and E. Heyn, "Ueber die Mikrophotographie in auffallenden Licht- und über die mikrophotographischen Einrichtungen der Kgl. mechanisch. technischen Versuchsanstalt in Charlottenburg." Mitteilungen aus den Kgl. technischen Versuchsanstalten, **1899**, 73. Also E. Heyn and O. Bauer, Metallographie, Sammlung Göschen, Leipsic, 1909, Vol. I.

FIG. 1.—Power saw.

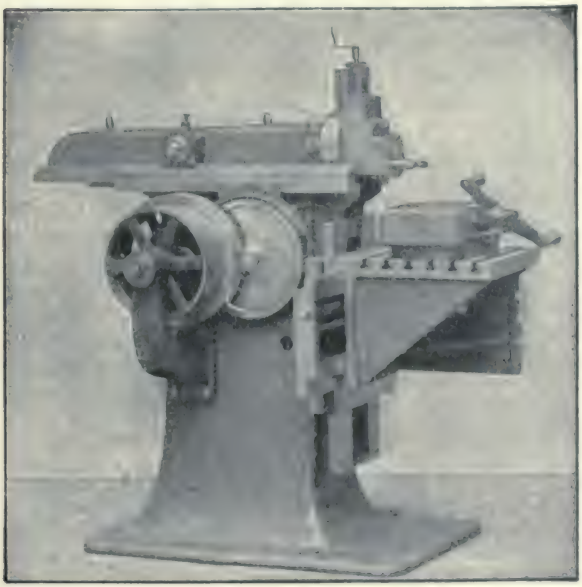


FIG. 2.—Planer.

the direction of the metallographist in charge. For taking samples with small cross-section it is desirable to have in the metallographic laboratory a small power saw, similar to that shown in Fig. 1, and a planer like that shown in Fig. 2. Normal rail sections can be worked conveniently on these machines. The saw and the planer are also useful in getting samples for chemical analysis.

2. Grinding and Polishing.—An old turning lathe, no longer used for other work, can usually be found in the work shop and answers very well for a grinding and polishing machine. Grinding is accomplished by means of wooden disks, built up from several layers of wood and covered with emery paper. Carpenters' glue can be used for fastening the paper to the grinding disks. The disks are fastened to the spindle of the lathe as shown in Fig. 3.[1] The diameter of the disk should be such that the largest surface to be examined can be ground at one time if possible. For practical reasons, a diameter of more than 340 to 360 mm. (13.4 × 14.2 in.) is not to be recommended because a test specimen of much larger area would be too heavy to handle and, moreover, French emery paper is usually sold in 450 by 340 mm. sheets. If the polishing disks are much larger than the sheets of emery paper, the grinding surface must be covered with several pieces pasted side by side and it is so difficult to make the adjoining sections fit exactly that the resulting surface is rarely smooth enough.

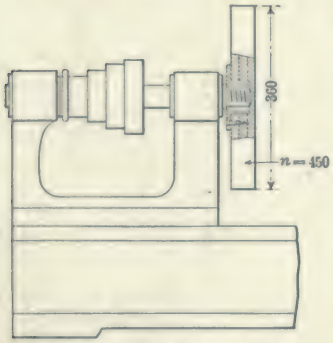


FIG. 3.—Polishing lathe.

When the old paper is used up a new piece is pasted on top of it. This may be repeated until the surface becomes uneven,

[1] The apparatus for smoothing and polishing described here has been used for many years in the Kgl. Materialprüfungsamt at Gross-Lichterfelde and was devised by Martens and Heyn. More recently disks of cast iron, brass, etc., have been used. With metal disks the emery paper is stuck on with a mixture of two parts of gelatin and one part of starch. After using the paper can be washed off with hot water.

after which the surface is turned down on the lathe and a new sheet glued on to the freshly exposed surface of the block.[1] French emery paper is furnished in eight sizes: Numbers 3 (coarsest), 2, 1C, 1M, 1F, 0, 00 and 000. Papers from numbers 3 to 0 should be used dry but when the finest numbers are used the grinding surface should be moistened with a few drops of machine oil, free from acid. American emery cloth may be used for the preliminary work, stopping with No. 00, which is coarser than No. 0 in the French sizes, and finishing with 0, 00 and 000 French emery paper.

In ordinary work it is not necessary to use all the grades of paper. The number of disks needed depends on the hardness of the specimen to be polished. The piece should be held lightly against the revolving disk until the scratches produced by the preceding, coarser disk have disappeared.

The final polishing is done on disks covered with broadcloth, using rouge (ferric oxide) and water. Commercial polishing rouge is fine enough for use without special treatment. It is stirred up with water to a paste in a large vessel and applied to the cloth with a brush.

The specimen is ready when it has a perfectly smooth mirror surface. The rouge adhering to the surface is washed off with running water, the water removed by alcohol and the surface finally dried with a soft cloth of cotton wool.[2]

3. The Microscope.—In many cases the chemist can distinguish inequalities in the composition of iron and steel without the aid of a microscope (*e.g.*, the formation of zones due to ex-

[1] Various firms, for example, "Vereinigte chemisch-metallurgische und metallographische Laboratorien," Berlin, C. 19, Adlerstrasse 7; and P. E. Dujardin & Co., Düsseldorf, Breitestrasse 71, furnish machines built especially for grinding and polishing metals and alloys. The use of a turning lathe as a polishing machine has the advantage, however, that it can be used as a lathe for the simple mechanical work that often has to be done in a laboratory. For a laboratory assistant, it is a good plan to have a reliable mechanic who is familiar with the use of the lathe, saw, and planer and who can be trained to grind and polish specimens, take turnings or borings for analysis and do the other mechanical work that is necessary in a chemical and metallographic laboratory.

[2] Detailed directions for grinding and polishing are given in "Metallographie," Heyn and Bauer, Göschen Collection, No 432, and in "Metallography," Desch, p. 136.

treme segregation) because marked irregularities of this sort can be seen with the naked eye if the specimen is properly treated. (See section *C*.)

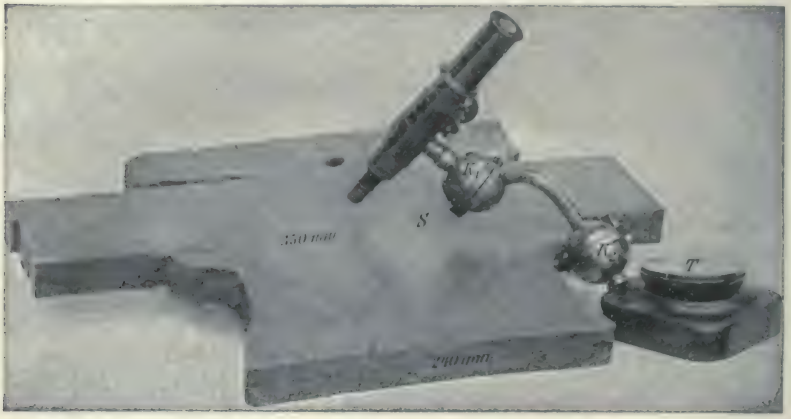


FIG. 4.—Microscope with Marten's ball and socket support.

This study of sections with the unaided eye has been called by Heyn "Macroscopic Analysis."[1]

FIG. 5.—Diagrammatic sketch of Fig. 4.

In other cases where it is a question of slight local differences, intentional or unintentional changes in chemical composition due to cementation, tempering, burning, etc., the microscope is indispensable. For a metallographic laboratory intended primarily to help the analyst in the selection of samples, a complicated and expensive microphotographic outfit is unnecessary. The microscope shown in Fig. 4 is satisfactory. (The Marten stand with ball and socket joint.)

Fig. 5 is a sketch of the optical principle involved. The specimen (*S* in Fig. 4) is placed in a position inclined to the optical axis of the microscope and illuminated by obliquely falling, diffused daylight. The mirror surface of the specimen reflects the incident ray in the axis of the microscope. With

[1] Mitt. a.d. Kgl. Materialprüfungsamt, 1906.

this arrangement, of course, only a small strip of the specimen is in focus while the rest is blurred, but as the microscope stand has two socket joints (K_1 and K_2 in Fig. 4) it is possible to put the microscope in any desired position so that the whole surface, even of a large specimen, can be examined without difficulty. The table, T, on which small specimens can be laid is also on a socket bed so that it can be placed at any angle with reference to the microscope.

Objective A and eyepiece 2 can be recommended as suitable and sufficient lenses for the analyst.[1]

[1] This microscope can be furnished by Carl Zeiss, Jena. The lens numbering is according to the Zeiss catalog.

CHAPTER III

TREATMENT OF THE POLISHED SPECIMENS

In some cases grinding and polishing alone are enough to show the distribution of certain constituents in the material. (See graphite, p. 17.) In most cases, however, further treatment is needed to develop the structure. For this purpose, the various etching methods are of chief importance.

Of the many etching mediums recommended in the literature only two will be mentioned here which if used intelligently will give the chemist ample information as to whether the material is or is not homogeneous.[1] These etching mediums are:

1. Copper ammonium chloride (E. Heyn) for the macroscopic study.

2. Alcoholic hydrochloric acid (A. Martens and E. Heyn) for microscopical examination.

For the detection of sulfide inclusions the method of

3. Printing on silk (Heyn and Bauer) is often useful.

1. Etching with Copper Ammonium Chloride (Method of Heyn).—Copper ammonium chloride has an electrolytic action on iron. An interchange takes place between copper ions in the solution and the iron of the specimen whereby spongy copper deposits on the surface of the specimen and an equivalent amount of iron goes into solution. The action is allowed to continue for from 1 to 2 min. and then the copper deposit is wiped off. To prepare the solution, use 120 cc. of water for each 10 g. of copper ammonium chloride (commercial). It is advisable to make up a large volume of the solution (10 or 12 liters) as the solution will keep indefinitely. The commercial salt is usually somewhat impure and will not give a clear solution but one containing a fine, white precipitate which eventually settles to the

[1] There is no advantage in using a great many etching mediums; it is of far greater value to test as carefully as possible with a few reagents on widely differing materials, and in this way become thoroughly familiar with their characteristic behavior under varying conditions.

bottom of the bottle. This precipitate need not be filtered off as it does no harm in the etching process.

The method of etching is as follows:

First, clean the specimen by wiping it with a bit of cotton soaked in absolute alcohol to remove traces of oil or grease (due to contact with the fingers) and then dip it under the etching solution with the polished surface up in a large flat dish of glass, porcelain or papier-mâché[1] as shown in Fig. 6.

Care must be taken to introduce the specimen into the solution in such a way that an even flow of liquid over the polished surface takes place, otherwise streaks and spots are likely to occur. Air bubbles on the polished surface must also be avoided. Wherever air bubbles stick, the copper will not deposit so that small, round, bright spots will be left on the otherwise etched surface. The etching medium must be kept in constant motion, either by stirring or shaking, from the time the specimen is put in until it is taken out again. If this is not done, especially with large surfaces, concentration changes take place in different parts of the solution which may cause a stronger attack at some places on the surface than on others and hence lead to quite false conclusions.

FIG. 6.—Etching dish with section.

If the etching solution is of the proper concentration (1:12)[2] and the temperature is not too low (room temperature of 16° to 18° C. is about right) the copper deposit can be removed easily by placing it under running water and wiping with cotton wool. Rinse the specimen with absolute alcohol to remove all traces of water and finally dry it by patting it gently with a soft, dry towel. Alcohol should be used liberally. Too great an economy in its use is always followed by the rusting of the test specimens. If, however, the water is completely removed the sections will keep indefinitely in a desiccator.

Etching with copper ammonium chloride is chiefly useful for the macroscopic study. It is especially suitable for soft iron, for

[1] Papier-mâché dishes are recommended because of their durability.

[2] Too strong solutions attack the specimen too quickly while if the solution is too weak the copper adheres so firmly to the iron that it is difficult to remove it.

ordinary carbon steel which has not been hardened, for white cast iron and above all for the detection of phosphorus segregation in castings.

The reagent is not suitable for graphitic irons as, on account of the galvanic action of the graphite, the copper deposits very firmly on the surface of such polished materials. Special steels, *e.g.*, nickel steel and chrome-tungsten steel, also cause the copper to deposit in a solid form.

2. Etching with Alcoholic Hydrochloric Acid (Method of Martens and Heyn).—Unlike the copper ammonium chloride solution, the alcoholic hydrochloric acid acts as a pure solvent. Certain components of the iron carbon alloy are more strongly attacked than others so that a specimen etched with alcoholic acid resembles one polished in relief;[1] some of the constituents appear to be raised above the others. This is one of the advantages of this reagent.

The solution is composed of 10 cc. hydrochloric acid (sp. gr. 1.2) in 1000 cc. of absolute alcohol.

As this solution will also keep indefinitely, it is well to make up a large quantity (5 to 10 liters).

Etching is carried out exactly as with copper ammonium chloride[2] except that the time of etching is considerably longer. With soft steels 3 to 15 min. are necessary and with hard steels the time may be considerably longer. In general, the etching should be stopped when the original mirror surface becomes dull. A quick inspection under the microscope will show whether the etching has gone far enough. If the etching is incomplete, replace the specimen in the bath. Constant motion of the etching solution is necessary in this case also. When the etching is complete, remove the specimen, without first washing it with water (as in the case of copper ammonium chloride treatment), rinse it with absolute alcohol and finally dry it on a soft towel.

Etching with alcoholic hydrochloric acid has for its main object the preparation of the specimen for microscopic analysis. It is well adapted for use with all kinds of iron and steel whether hardened or not. It is not suitable, however, for indicating phosphorus segregations. Special steels (nickel steel, chrome-

[1] For a discussion of relief polishing see "Metallographie," Heyn and Bauer.

[2] Papier-mâché dishes are not recommended for this reagent.

tungsten steel, etc.) are very slowly attacked by this reagent. The effect can be increased somewhat by the addition of a few cubic centimeters of picric acid solution (5 per cent. in alcohol).

3. Printing on Silk as a Test for Sulfides (Heyn and Bauer).—The method of taking a sulfur print depends on the fact that sulfur occurs in iron and steel chiefly as iron sulfide or manganese sulfide, both of which evolve hydrogen sulfide on being treated with dilute hydrochloric acid.

The method is as follows:

Cover the polished surface with a piece of silk and then by means of a small brush or wad of cotton, moisten the silk with a solution of the composition:

10 g. mercuric chloride.
20 cc. hydrochloric acid (1.12).
100 cc. distilled water.

Wherever sulfide inclusions are present, hydrogen sulfide is evolved and will cause black mercuric sulfide to deposit on the silk. The action should be allowed to continue for 4 or 5 minutes.

The brisk evolution of hydrogen that takes place during the reaction is likely to cause the formation of bubbles under the thin piece of silk. Press out the bubbles, as fast as they collect, by means of a brush soaked with the solution. Take pains throughout the whole process to keep the thin silk sheet in close contact with the polished surface. Replace the exhausted solution with fresh solution, from time to time, by brushing the surface with wet cotton.

After the action is complete, remove the silk cloth and wash it with tap water to take out the acid. If this washing is carried out carefully, none of the black, firmly adhering mercuric sulfide will be lost. The silk sheet then shows an exact mirror image of those spots on the surface of the specimen where sulfide inclusions occur.[1]

[1] Phosphorus-rich spots generate phosphine under the action of hydrochloric acid. This deposits lemon-yellow mercuric phosphide when brought in contact with mercuric chloride solution. There is no danger of confusing such a precipitate with the sulfide deposit and, moreover, the evolution of phosphine is very slow in comparison with the evolution of hydrogen sulfide.

The method gives satisfactory results, especially where the included sulfide is closely segregated. If the sulfur content is small and uniformly distributed in the mass, the silk assumes a pale gray color with no clearly marked spots.[1]

[1] A modification of this method was suggested by Baumann (Metallurgie, 1906, 416).

CHAPTER IV

METALLOGRAPHIC CHARACTERISTICS OF THE CONSTITUENTS OCCURRING IN IRON AND STEEL

1. Graphite, Temper Carbon (Pure Carbon.)—Etching of the polished specimen is not necessary for the detection of graphite in iron or for the detection of the temper carbon, which cannot be distinguished from it chemically. Graphite appears under the microscope, or can often be seen with the unaided eye, in the shape of dark gray or black veins[1] of varying length and thickness. The shape, size, and arrangement of the veins depend on the manner of formation and on the kind of iron.

Fig. 7 shows on the left half (magnified 117 diameters) clusters of graphite needles, while the right half shows the long graphite veins.[2] The sections were not etched but simply ground and polished. Temper carbon occurs usually, though not always, in the shape of round spots, gray or black in color. Fig. 8 (magnified 350 diameters) shows a tempered specimen. The section was etched with alcoholic hydrochloric acid. The dark round spots are temper carbon.

2. Ferrite.—(Carbon-free iron, which forms a solid solution with many other substances, *e.g.*, with phosphides, manganese, silicon and nickel.)

Etching with Copper Ammonium Chloride.—Macroscopically, or with slight magnification, the individual ferrite grains seem to be slightly roughened and are more or less lustrous, depending on the direction from which the light comes. With stronger magnification it will be seen that roughening of the grains is due to etch-figures[3] and that there is a definite orientation of

[1] In reality the graphite veins correspond to sections of larger or smaller graphite plates.

[2] The two sides of the figure represent different kinds of iron.

[3] See E. Heyn, "Mikroskopische Untersuchungen an tiefgeätzten Eisenschliffen," Mitt. d. Kgl. techn. Versuchsanstalten, **1898**, 310.

M = 117

FIG. 7.—Graphite in iron.

M = 350

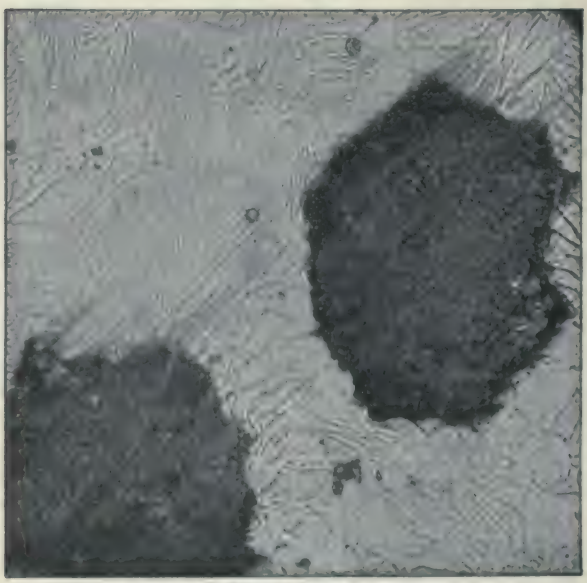


FIG. 8.—Temper carbon in iron.

the etch-figures on each grain. These lines are characteristic of ferrite, and give in addition a means of distinguishing clearly the boundaries between the crystals.

The left half of Fig. 9 shows the roughened appearance of the ferrite grains due to etch-figures. The linear magnification is 350. The right half of the figure gives a magnification of 1650 diameters and shows clearly the symmetrical arrangement of the etch-figures in the individual ferrite crystals.

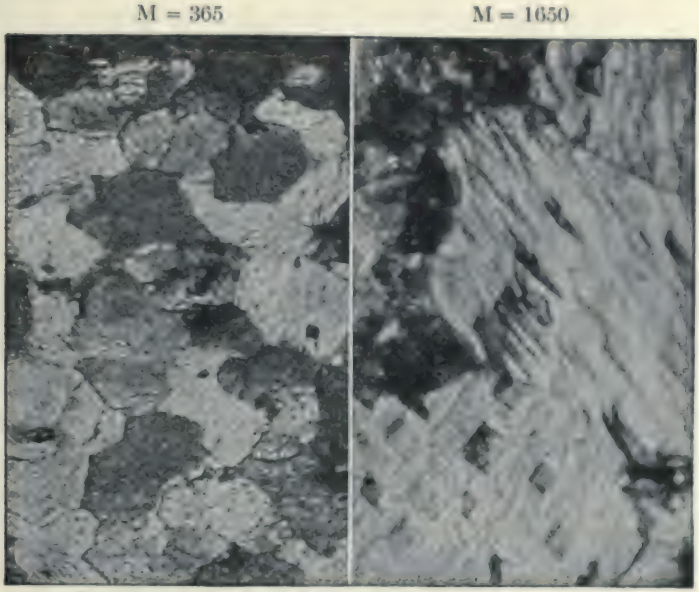


FIG. 9.—Ferrite.

ETCHING WITH ALCOHOLIC HYDROCHLORIC ACID.—Ferrite is much less strongly attacked with this reagent than when copper ammonium chloride is used. Etch-figures are formed only after action has gone on for some time and even then are quite indistinct. If the etching is allowed to go on for only a little while, the ferrite is not colored but if the treatment goes on for a longer time some of the ferrite grains appear slightly yellow.

3. Cementite.—(Iron carbide, Fe_3C with 6.67 per cent. carbon; forming solid solutions, or double carbides, with other carbides

e.g., with manganese carbide or chrome-tungsten carbide.) Cementite is not attacked appreciably either by copper ammonium chloride or by alcoholic hydrochloric acid; after etching, therefore, the specimen is still uncolored and with its mirror surface untarnished. Cementite for this reason, cannot be mistaken for ferrite. Because of its resistance to etching reagents, it is left in relief with respect to ferrite and pearlite. Fig. 10 (magnified

M = 1650

FIG. 10.—Cementite and pearlite.

1650 diameters) shows the structure of white cast iron. The light part is cementite, the ground mass pearlite.

4. Pearlite.—(Eutectic mixture of ferrite and cementite. The temperature of formation in the case of the iron carbon alloys is about 700° C. Pearlite contains about 0.95 per cent. carbon.)

The microscopic structure of pearlite depends to a great degree on the rate at which it passes on cooling through its

transition point (700° C.).[1] If the rate of cooling is slow, distinct plates of ferrite and cementite are formed, while if the rate of transformation is increased, a series of transition products is formed ranging from pearlite through sorbite, osmondite and troostite to martensite. (See below.) Inspection of the pearlite shows within certain limits whether the material was cooled slowly or quickly through the transition temperature.

Etching with Copper Ammonium Chloride.—Pearlite appears very dark after etching, so that it is often possible to distinguish between the parts rich in carbon (pearlite spots) and the locally decarbonized portions (pearlite-free spots) without the aid of a microscope.

The dark color is in reality only an apparent one as neither cementite nor pure (phosphorus-free) ferrite is colored by copper ammonium chloride. The darkening depends on the production of a relief structure by etching. Since cementite is not at all attacked and ferrite is dissolved to a considerable extent, marked differences in the height of the individual lamellæ are produced, and, in addition to this there is the roughening of the ferrite plates due to the etch-figures. More or less intense shadows are formed as shown in the sketch, Fig. 11, the depth of the shadow depending on the direction of the light. These shadows make the whole pearlite field appear dark even though it is distinctly laminated.

Fig. 11.

As the dark color after etching with copper ammonium chloride may be due to other causes (high phosphorus content, a sudden passing through the critical temperature, permanent change of shape in the cold)[2] it is always advisable to follow the macroscopic study with a microscopic one.

Etching with Alcoholic Hydrochloric Acid.—With low magnifications pearlite shows a darker color than ferrite[3] although the difference is not so strongly marked as with copper ammonium chloride.

[1] *cf.* E. Heyn, Z. Elektrochemie, **1904.**

[2] E. Heyn, Mitt. a.d. Kgl. Materialprüfungsamt, **1906,** Part 5.

[3] In case sorbitic pearlite is not present the dark color is explained as in the case of etching with copper ammonium chloride.

With stronger magnification the separate lamellæ of ferrite and cementite can be distinguished. The left half of Fig. 12 (magnified 123 diameters) shows an iron with 0.44 per cent. carbon. The dark masses are pearlite and the light ground mass ferrite. The right half of the figure shows the same iron at 1650 diameters. The single lamellæ of ferrite and cementite are clearly marked and the photograph also shows that neither constituent is dark colored. The shadows in the pearlite are, however, readily distinguished.

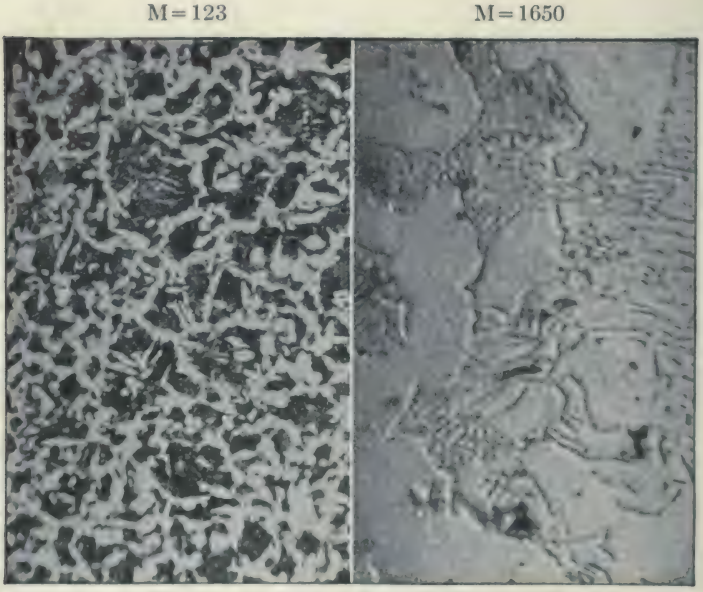


FIG. 12.—Pearlite and ferrite.

A very close estimate of the amount of carbon in any part of the surface can be made from a study of the comparative size of the ferrite and pearlite areas. If x represents the estimated per cent. of pearlite (more accurately found by planimetric measurements) then, since pearlite contains 0.95 per cent. carbon, the per cent. by weight of carbon in the iron is $0.0095x$. Such an estimate is often fairly accurate.

5. Austenite.—(Solid solution of iron carbide in γ-iron.) Austenite is obtained when a steel with high carbon content

is quenched as quickly as possible from a high temperature. Manganese favors the formation of austenite. In general, *e.g.*, in low manganese steel, pure austenite is not formed but a mixture of austenite and martensite.

Copper ammonium chloride is not suitable for etching quenched (hardened) steel because the copper deposits so firmly on the polished surface that it is difficult to remove it.

Etching with Alcoholic Hydrochloric Acid.—Austenite is not at all attacked but remains white and brilliant. Fig. 13 (magnified 100 diameters) shows a steel with 1.3 per cent. carbon, quenched in water from 1180° to 0°. The lighter, unattacked surfaces are austenite while the darker needle-like masses are crystals of martensite.

M = 365

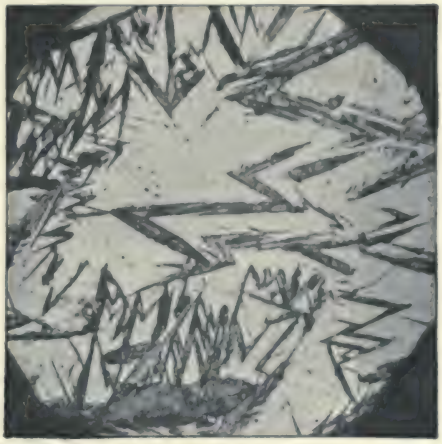


Fig. 13.—Austenite and martensite.

6. Martensite.—This structure element represents the beginning of the decomposition of the solid solution of iron carbide in γ-iron. Pure martensite is obtained only after sudden quenching.

Etching with Alcoholic Hydrochloric Acid.—The characteristic of martensite is its needle-like structure, which becomes more strongly marked the longer the etching is continued. Some of the needles are much more strongly attacked than others and as a result a marked roughening of the surface of the specimen is produced. Pure martensite is uncolored and lustrous even after long-continued exposure to the etching solution. Fig. 14 (magnified 875 diameters) shows pure martensite obtained by very rapid cooling of a carbon steel with about 1 per cent. C. If the cooling is less sudden or not uniform, more or less dark spots, veins and other forms appear, corresponding to the transition constituents to be described in the next section.

Fig. 15 (magnified 117 diameters) shows a uniformly quenched

steel with 0.95 per cent. C. The light ground-mass is martensite and the dark spots are troostite.

M = 875

FIG. 14.—Martensite.

7. Troostite, Osmondite, Sorbite.[1]—(Transition constituents between martensite and pearlite.)

If the quenching is not so rapid that martensite can form and, on the other hand, not slow enough to allow the formation of pearlite, transition products between martensite and pearlite appear. The same components are formed when a quickly cooled piece is slowly reheated (annealed). In this way, however, a definitely characterized intermediate product, osmondite, is passed over, which corresponds to an annealing temperature of 400° with tool-steel having 1 per cent. carbon. Those transition forms which are nearest to martensite (corresponding in tool steels to an annealing temperature between 0° and 400°) belong to the troostite group while those nearer pearlite (annealed between 400° and 700°) are of the sorbite class. Between the two (at 400°) is osmondite.

M = 117

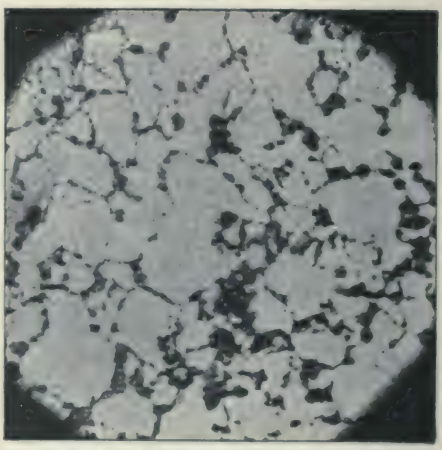


FIG. 15.—Martensite and troostite.

[1] *cf.* Heyn and Bauer, Mitt. a.d. Kgl. Materialprüfungsamt, **1906**, 529.

ETCHING WITH ALCOHOLIC HYDROCHLORIC ACID.—A characteristic indication is the degree of darkening caused by etching with this reagent. Pure martensite is scarcely colored at all, the darkening increases as the annealing temperature is raised (troostite), reaching a maximum at 400° (osmondite) and then decreasing toward the pearlite side (sorbite). The solubility in dilute sulfuric acid shows a corresponding variation.

Fig. 16 shows the effect of etching with alcoholic hydrochloric acid on a 0.95 per cent. carbon steel, quenched from 900° and then annealed at different temperatures.

The characteristic structure elements are indicated in the following table.

Troostite:	The needle-like structure is still visible with some of the needles dark and others much lighter. The dark color increases with increasing annealing temperature. See Fig. 17 (magnified 350 diameters), steel with 0.95 per cent. carbon, quenched at 900° and annealed at 275°.
Osmondite:	The needle structure is no longer evident. The dark color has reached its maximum. See Fig. 18 (magnified 350 diameters), steel with 0.95 per cent. carbon, quenched from 900° and annealed at 405°.
Sorbite:	Small, unformed islands of cementite are visible. The dark color decreases with increasing annealing temperature. See Fig. 19, steel with 0.95 per cent. carbon, quenched from 900° and annealed at 640°.

8. Ledeburite.—(Solid solution of 4.2 per cent. carbon in the cementite eutectic; solidification temperature, about 1130°.)[1] Ledeburite is made by the sudden quenching of white cast iron during or immediately after its solidification. Alcoholic hydrochloric acid attacks the plates of solid solution (with about 1.76 per cent. carbon) exactly as it does martensite, while the cementite lamellæ are unaffected. Fig. 20 shows the structure of white cast iron quenched from 1087° with a magnification of 350 diameters. The ledeburite is coarse in structure while the solid solution shows the martensitic structure. Near the ledeburite

[1] *cf.* F. Wüst, Metallurgie, **1909.**

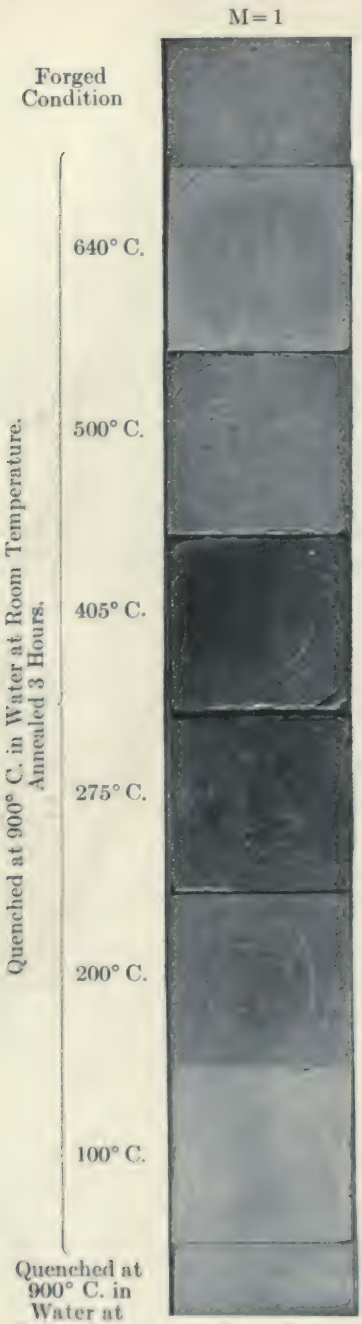


FIG. 16.

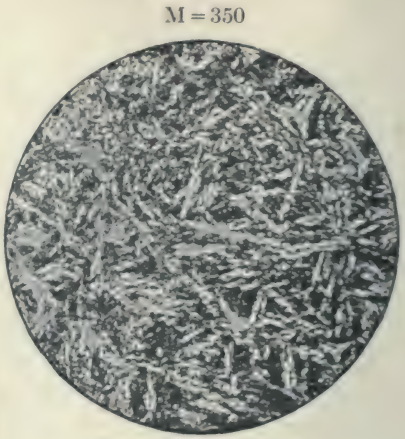


FIG. 17.—Troostite

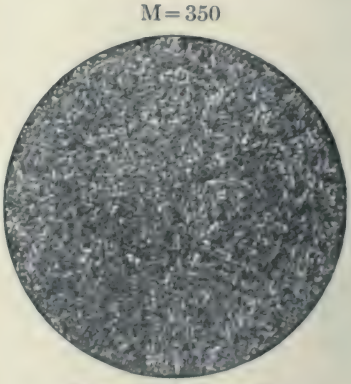


FIG. 18.—Osmondite.

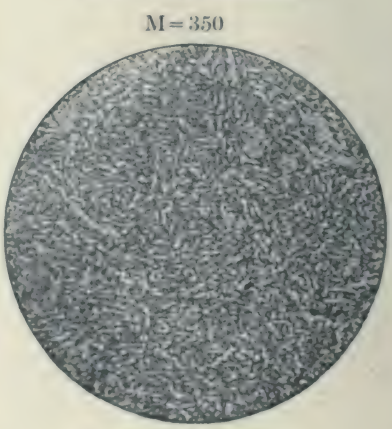


FIG. 19.—Sorbite.

eutectic may be seen a few dark-colored, troostite-like, transition forms.

9. Phosphorus Segregations in Iron.—Phosphorus occurs in iron as phosphide (Fe_3P).[1] Iron free from carbon can retain about 1.7 per cent. phosphorus in solid solution. With increasing carbon content the solubility of the phosphorus in the iron decreases. The crystals of solid solution which are rich in phosphorus are usually more coarsely crystalline than the crystals which contain less phosphorus.

FIG. 20.—Ledeburite and solid solution (Martensite).

Fig. 21 (magnified 4 diameters) shows a strip of these coarse crystal grains with high phosphorus content. A coarse-grained structure is not in itself proof of a high phosphorus content, as the size of the ferrite crystals depends largely upon the heat treatment that the material has undergone.

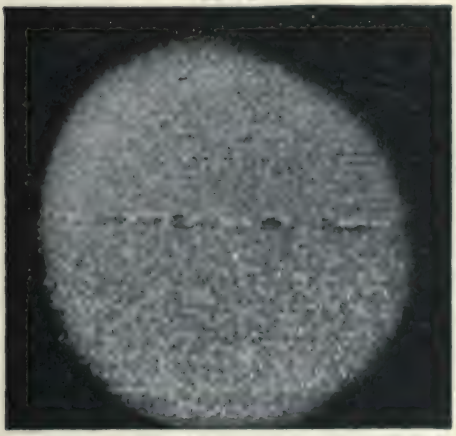


FIG. 21.—Coarsely crystalline ferrite rich in phosphorus.

Etching with copper ammonium chloride is very useful for detecting the segregation of phosphorus in iron and steel. This reagent darkens the solid solution that is rich in phosphorus, forming a stain which varies in color from dark brown to bronze.[2]

[1] Stead, Iron and Steel Institute, **1900.**

[2] Heyn assumes that this is due to copper phosphide.

The specimens shown in Figs. 70 to 75 were all etched with copper ammonium chloride. All show a more or less dark colored inner zone, with an outer area appearing much lighter. The chemical analysis of these specimens illustrates the fact that there is an intimate connection between the dark color and the phosphorus content. The color of the dark zone is so characteristic that an expert is very rarely in doubt as to whether the darkening is due to phosphorus or to something else.

A less experienced observer might possibly confuse the dark spots due to high phosphorus with areas that are rich in carbon, as these also appear somewhat darker after etching. Such a mistake is not possible if a higher magnification is used because of the large amount of pearlite present in the areas which are rich in carbon. (See p. 22.) In places where a mild steel has been subjected to cold deformation, dark spots may also occur, *e.g.*, in the neighborhood of punched rivet holes.[1] An examination of the ferrite grains with high magnification gives the reason for this darkening. The individual particles of ferrite show distortions, etching furrows, etc., so that here too there is not much danger of mistaking a dark spot of this type for a phosphorus spot.

Phosphorus occurs in cast iron as the free phosphide (Fe_3P). Simple etching does not suffice to distinguish it from cementite (Fe_3C) because phosphide of iron, like the carbide, is not attacked strongly by the etching medium, so that both compounds remain white and brilliant. Heat tinting,[2] however, gives a ready means of distinguishing between the two, as the tint produced by heating the carbide is always a few stages in advance of the phosphide color.[3] The order of the heat tints produced with rising temperature is yellow, orange, red, purple, blue, etc. When the cementite is purple, for instance, the phosphide will still appear yellow.

10. Sulfide Inclusions in Iron.—As already mentioned on p. 15, sulfur occurs in iron as ferrous sulfide or as manganese sulfide. Since neither of these sulfides forms a solid solution with iron, it is possible to recognize very small amounts of sulfide under the

[1] *cf.* E. Heyn, Z. Ver. Deutsch. Ing., **1900.**

[2] Heyn and Bauer, "Metallographie," Sammlung Göschen.

[3] *cf.* Wüst, Metallurgie, **1908,** 3–85.

M = 117

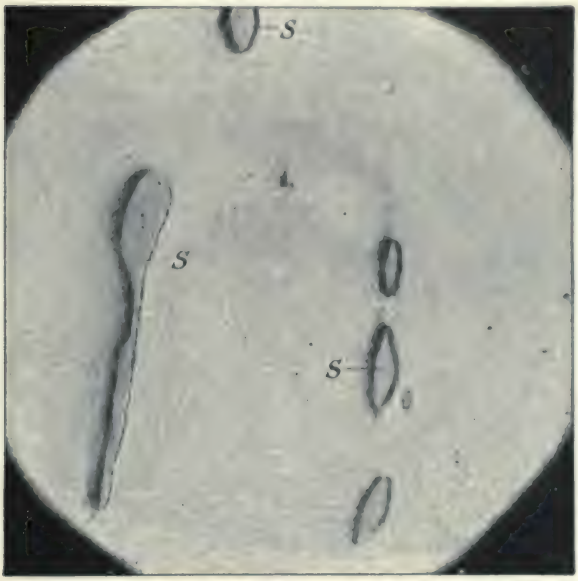


FIG. 22.—Sulfide inclusions in ingot iron.

microscope. They appear chiefly as round, or in rolled material as elongated, spots varying from fawn color to pale blue. They are not attacked by copper ammonium chloride. Dilute acid dissolves the sulfides with evolution of hydrogen sulfide. Fig. 22 (magnified 117 diameters) shows some sulfide inclusions in mild steel. When other non-metallic inclusions (*e.g.*, slag or oxides) are present, it is often hard to recognize sulfide. For its detection under these conditions, a sulfur print on silk (p. 15) is very useful.

M = 1

FIG. 23.—Sulfur print on silk.

M = 350 M = 350

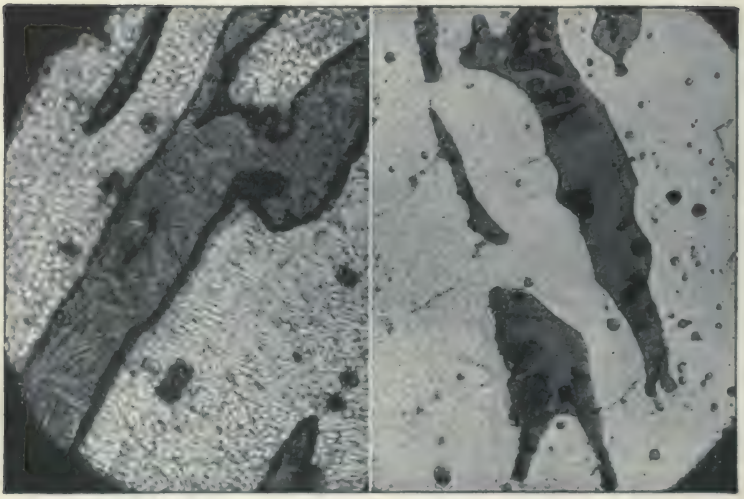


FIG. 24.—Slag inclusions in wrought iron.

Fig. 23 shows a sulfur print in natural size. The dark streaks and spots correspond to sulfide inclusions in the sample.

M = 365

FIG. 25.—Non-metallic inclusions in ingot iron.

11. Other Non-metallic Inclusions.—In the case of wrought iron it is known that the non-metallic material is almost wholly slag. Wrought-iron slag inclusions are usually characterized by their dark-gray to bluish-gray color. With large inclusions it is often noticeable that they are not homogeneous and sometimes well-formed crystallites of a lighter tint are visible. (*cf.* The left half of Fig. 24, magnified 350 diameters.)

In other cases round spots of a shade darker than the ground mass are noticed. (*cf.* The right half of Fig. 24, magnified 350 diameters.) These differences in structure suggest different states of oxidation of the iron in the slag.

In the case of ingot iron or ingot steel, the nature of the non-metallic inclusions is not known positively.[1] The inclusions may have a very different composition and very different appearance, depending on the method of manufacture, the deoxidizing material used, and other conditions. In nearly all cases, however, they differ markedly in appearance from the slag inclusions found in wrought iron. Fig. 25 (magnified 365 diameters) shows a coarse group of non-metallic inclusions in a plate of ingot iron. The photograph also shows that the inclusions are not all alike, the mass being made up of at least three structure elements.

Although the nature of these inclusions in ingot iron or steel is not clearly understood, it is nevertheless possible in nearly every case to determine whether the material is wrought iron or not by the appearance of the inclusions.

Etching is not necessary for the study of non-metallic inclusions. Large masses of slag are visible to the naked eye, both in wrought iron and in ingot iron or steel as dark spots on the mirror surface. For evidence of smaller inclusions, the microscope should be used, as otherwise rouge spots and other accidental impurities on the polished surface might be mistaken for slag and non-metallic inclusions.

[1] *cf.* B. W. Rosenhain. 5. Internationaler Kongress für Materialprüfung in Kopenhagen (1909); also H. Hibbard, Bull. of the American Institute of Mining Engineers, **1911,** No. 52, p. 325.

CHAPTER V

THE CAUSES OF LOCAL DIFFERENCES IN THE CHEMICAL COMPOSITION OF IRON AND STEEL

In Chapter I it was pointed out that intelligent sampling was of great importance because the composition of the sample is not necessarily uniform throughout its entire cross-section. The reasons for these local differences are numerous.

1. They may depend on the method of preparing the material and are often unavoidable. To this class belong the irregularities due to segregation. Such irregularities may persist throughout all the steps that the material undergoes in its manufacture and often make sampling exceedingly difficult. In cast iron, the rate of solidification and the rate of cooling after solidification play an important part in the amount and form of the graphite that separates out. Large castings harden and cool more slowly than small castings and the same holds true for different sections of the same castings. The slower the cooling, the more graphite is deposited and conversely.

2. They may be produced intentionally in the working of the material. In such cases the manufacturer has in mind the preparation of materials for specific purposes. Cementation, tempering, case hardening, etc., produce local differences of this nature.

3. The irregularities in composition may be produced unintentionally and without the knowledge either of the maker or user, by processes of manufacture or by subsequent use (*e.g.*, decarbonization due to burning the steel, decomposition phenomena, rusting, etc.). All these phenomena may be considered as representing diseased conditions of the metal. They are often the cause for the rejection of otherwise flawless material.

In all these and similar cases, the analyst is dependent on metallography for the recognition of local irregularities. In later chapters, concrete examples from actual practice will be given

to show how much the analytical results may be influenced under certain conditions by the local differences.

4. The way the sample is taken may have a marked influence on the results of the chemical analysis even though the material is itself uniform. The sources of error due to unskilful sampling will be indicated in the next chapter.

CHAPTER VI

TAKING SAMPLES IN THE WORKS

1. General Discussion of Sampling.—As a general rule for all metals that can be worked with a cutting tool, a better representative sample can be obtained by *planing* over the whole cross-section than by drilling, turning, etc., and when a metallographic study has preceded the chemical analysis, the shavings should be taken from the place adjoining that from which the specimen was taken for microscopical study. Fig. 26 shows the method used in taking a sample from a steel rail.

If marked irregularities are found by the microscopic study, it may be desirable under certain conditions to get samples from different parts of the specimen, in which case drilling, turning, etc., may be necessary. If merely an average analysis is required, however, planing of the whole surface is enough. In reporting a complete analysis, an exact statement should be given of the method of sampling, with an explanatory sketch if necessary. A sketch is indispensable if shavings have been taken from different parts of the specimen (core, outer zone, etc.).

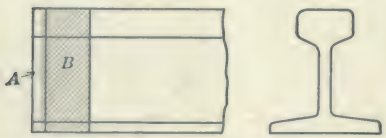


FIG. 26.—*A*. Section for metallographic study. The surface indicated by the cross-hatched line is ground, polished and etched. *B*. Shavings for analysis are obtained by planing the whole cross-section.

Frequently, far too little care is taken with the purely mechanical part of taking samples, cleaning of the test specimen, planing and collecting samples, in spite of the fact that many serious errors can be introduced by careless work. The first requisite is naturally that the planer should be clean, that no shavings from previous tests are on it, and that all parts that come in contact with the specimen are free from oily, fatty, or soapy matter. Care must also be used to see that no oil or grease drops on the shavings already made.

2. Cleaning the Surface of the Test Piece.—Before taking a sample the surface of the piece must be examined carefully for external impurities and freed from any that may be found. First come the substances that adhere loosely, *e.g.*, saw-dust from the packing, dirt, in case the specimen has lain on the ground, and similar impurities. These can often be removed by washing or by rubbing with a stiff brush or polishing cloth. Paint or shellac, letters, numbers, as well as rust spots, can be removed by means of a wire brush or, if necessary, by using a solvent for the paint (alcohol, ether, gasolene, kerosene, etc.), but only those solvents should be used which do not attack iron.

Surface coatings produced during the manufacture, *e.g.*, casting skin, forge scale, etc., adhere much more firmly than accidental impurities. If they cannot be removed by the steel wire brush, it is necessary to hammer, file, or rub with emery cloth. In such cases care should be taken not to remove large quantities of material.

3. Planing and Collecting the Shavings.—If the material is hard, the speed of the planer should not be too fast or the tension too high, as otherwise the shavings are apt to fly off and be lost and there is the additional danger that pieces of the cutting tool may break off and contaminate the sample. If a piece of the cutting tool should fall into the sample and be weighed with it, incorrect results would be obtained without any reason apparent to the analyst. It is scarcely necessary to say that shavings which have fallen on the floor should not be used for analysis, as the chance of contamination is too great. The greatest care should be used in the taking and collecting of samples in the shop.

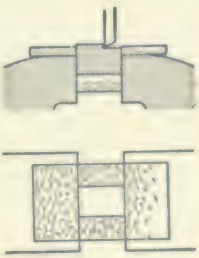


FIG. 27.

In planing certain kinds of iron, the untrained workman is likely to pick up only the coarser shavings, leaving the finely powdered material, *e.g.*, graphite in cast iron or slag in wrought iron, on the bench or even blowing it away. The fact that very serious errors can be introduced in this way will be shown on pp. 59 and 115.

To avoid losses it is a good plan to place strong, glazed paper

around the test piece, as shown in Fig. 27. Then, if the cutting speed and tension are properly chosen so that the shavings do not spring away during the planing, the coarse shavings as well as the powdery material will fall into the paper and, after the removal of the test piece, may be shaken into a bottle without any danger of loss.

4. Annealing before Taking the Sample.—Hardened steel is often annealed before planing, to make it more easily machined. The annealing temperature in the case of carbon steel is such that it will be above the pearlite point (700° with pure carbon steel). A quarter of an hour's annealing at 750°–800° followed by a slow cooling until the pearlite point is reached is enough. Below 600° the cooling can take place quickly, for with carbon steels even quenching in water will not noticeably increase the hardness in this temperature range.

The following table may serve as an aid in determining the approximate temperature.[1]

Dull red heat	about 525°–550°
Dark red heat	about 700°
Dull cherry red	about 800°
Cherry red	about 900°
Bright cherry red	about 1000°
Dark orange	about 1100°
Bright orange	about 1200°
White heat	about 1300°
Bright white heat	about 1400°
Dazzling white heat	about 1600°

The heating can take place in an open charcoal fire. If it is done in a furnace (tube furnace, muffle furnace, etc.), it is advisable, in order to avoid the formation of forge scale with a consequent superficial decarbonization, to place pieces of charcoal before and behind the test piece. The air entering the furnace must then pass over hot carbon so that the oxygen is burned to carbon monoxide. The formation of forge scale can be prevented almost entirely in this simple way. The fear that superficial carbonization (cementation) of the test piece can

[1] Exact temperature measurements are made with a thermo-element. For details concerning these measurements, consult "The Measurement of High Temperatures" by G. K. Burgess and H. Le Chatelier.

be produced in this way by the carbon monoxide is unfounded. A very much longer time would be required to produce an appreciable cementation effect.[1]

It should be stated that the presence of certain elements in the steel, *e.g.*, manganese and nickel, causes a material lowering of the pearlite point. In such cases care must be taken in the cooling after annealing.

5. The Sampling of Materials which Cannot be Machined.—Certain alloys and self-hardened steel cannot be machined with

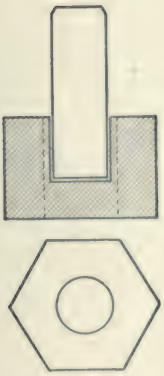


FIG. 28.

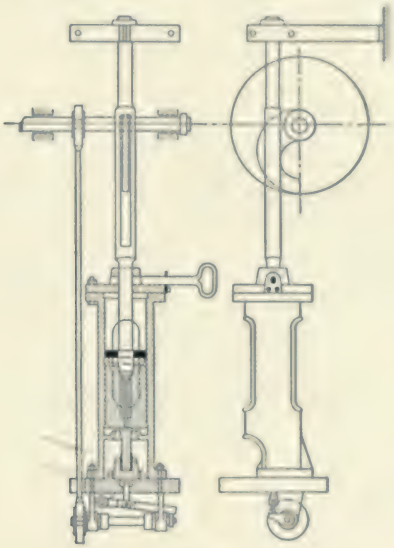


FIG. 29.

ordinary steel tools even after annealing and slow cooling. White cast iron cannot be annealed because of the possible separation of temper carbon. In some cases special tool steel can be used (chrome-tungsten and similar alloy steels). The usual precautions should be taken.

If, however, the material cannot be worked either with carbon

[1] *cf.* Bauer, Stahl u. Eisen, **1909,** No. 18. The author has never succeeded in detecting by metallographic means the slightest trace of superficial carbonization after 15 minutes annealing in contact with charcoal.

steel or any of the special steels, it is necessary to knock off small pieces from different parts of the sample and to pulverize these pieces. This can usually be done with a heavy hammer on a steel anvil. If the specimen is very large and heavy, a trip hammer is sometimes needed. To avoid scattering the small fragments, the sample should be wrapped in a piece of heavy linen cloth. If a trip hammer is used, a piece of iron should always be put between the test specimen and the hammer, to avoid possible injury to the machine. The broken pieces must be carefully cleaned to free them from linen fibers. The final powdering of the sample can be accomplished in a diamond mortar, the simplest form of which is shown in Fig. 28. A machine shown in Fig. 29 is useful for breaking up white pig iron.[1]

The powder obtained after treatment of the larger lumps is heaped up and sampled in the usual way (heaping and quartering).

6. Sampling of Material in Wire Form.—If the material is in the form of thick wire, it is beaten out on the anvil until it is in the form of thin sheets which can be cut with tin-smith's shears.[2]

Each wire is now cut into pieces of approximately the same length. For the final sample one or two of these shorter pieces from each coil are taken and after thorough mixing are cut into still smaller pieces for the final weighing. If there is doubt, or if the metallographic examination shows that the wires are not all alike, it is useless to take an average sample. In this case a number of small sections should be cut from the long wire and treated separately.

[1] A. Kaysser, Stahl u. Eisen, **1907**, 1353.

[2] If the wire is thin at the start, so that it is easy to cut, hammering is not necessary.

SECTION II

SPECIAL CASES. CONDITIONS WHICH MAKE THE TAKING OF REPRESENTATIVE SAMPLES DIFFICULT

CHAPTER VII

WHITE IRON, FERRO-MANGANESE, CHILLED CASTINGS, AND MALLEABLE CASTINGS

Where planing over the whole cross-section of the sample is impossible because of the hardness of the material, the question of getting an average sample from a large piece is always unsatisfactory unless the whole specimen can be broken into pieces, because if the piece is not homogeneous, it is difficult if not impossible to get an average sample by knocking off separate pieces. In such a case the analyst should always give the method of sampling with his report and, if necessary, state specifically that the analysis may not be absolutely representative.

1. Inequalities in the Composition of White Pig Iron and Ferro-manganese.—That, in actual practice, very marked differences

FIG. 30.

in the composition of white-iron and ferro-manganese may occur in different parts of the cross-section is shown in the following examples.

From each middle pig (of 15) of a ten-row casting bed, pieces were broken off from the center and edge on the same cross-section, as shown in Fig. 30, and analyzed for manganese and phosphorus. The results are shown in the following table.[1]

[1] C. Reinhardt, Repertorium der anal. Chem., **1887**, 742.

TABLE 1.—ANALYSES OF BASIC-BESSEMER PIGS, ACCORDING TO REINHARDT

Middle pig of the bed	Manganese		Phosphorus	
	Center, per cent.	Edge, per cent.	Center, per cent.	Edge, per cent.
1	2.33	2.33	2.17	2.56
2	2.43	2.54	2.14	2.54
3	2.54	2.64	2.11	2.62
4	2.69	2.79	2.03	2.41
5	2.74	2.85	2.34	2.50
6	2.79	2.85	2.12	2.50
7	2.85	2.95	1.98	2.21
8	3.00	3.00	2.09	2.30
9	3.00	3.00	2.38	2.38
10	3.16	3.16	2.43	2.69

The differences between the center and the edge are very marked, especially in the phosphorus content.

Similar results were obtained on the analysis of pigs *A* and *B* of different grades of basic-Bessemer pig. (See Table 2.)

TABLE 2.—ANALYSES OF BASIC-BESSEMER PIG, ACCORDING TO REINHARDT

Pig	Manganese		Phosphorus	
	Center	Edge	Center	Edge
A	2.72	2.43	2.56	3.09
B	3.52	3.57	2.60	2.76

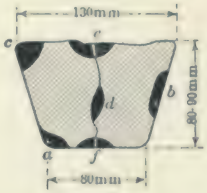


FIG. 31.

Reinhardt also analyzed pieces taken from the points marked *a*, *b*, *c*, *d*, *e*, and *f* shown in Fig. 31. The results were as follows:

TABLE 3.

Sample taken at	Manganese, per cent.	Phosphorus, per cent.
a	2.95	3.42
b	2.90	3.50
c	3.05	3.44
d	2.95	3.36
e	3.00	3.42
f	2.95	3.48

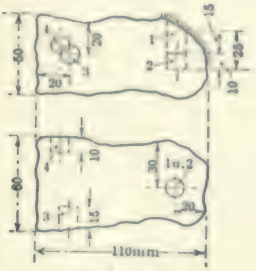


FIG. 32.

Hampe[1] studied the composition of different parts of a piece broken from a pig of ferro-manganese. He found the following manganese content at the points marked 1, 2, 3, and 4 in Fig. 32.

TABLE 4.—ANALYSES OF A FERRO-MANGANESE PIG, ACCORDING TO HAMPE

Sample taken at	Per cent., manganese
1	82.82
2	81.97
3	81.10
4	80.17

The differences in manganese content at different parts of the same section are considerable. Whenever the price of ferro-manganese is figured on the manganese content, the only way to correct for these variations within the pig is to take a mixed sample made up from pieces of a large number of pigs.

[1] K. Hampe, Stahl u. Eisen, **1893**, 392.

2. Formation of Globules and Nodules.—It happens not infrequently that in pig iron and in large castings, well formed globules or nodules, sometimes as large as a walnut and quite different from the rest of the metal in composition, separate from the matrix and remain inclosed in the pig or casting. Sometimes they are in close contact with the metal and at other times are contained in cavities in the casting. These inclusions are always much higher in phosphorus than the matrix but are lower in silicon. Platz[1] studied the composition of globules of this sort and found the following values:

TABLE 5.—ANALYSES OF GLOBULES AND NODULES ACCORDING TO PLATZ

	Gray iron with white edge			Mottled iron			Mottled pig iron	
	Globules, per cent.		Matrix, per cent.	Globules, per cent.	Nodules,[2] per cent.	Matrix, per cent.	Globules, per cent.	Matrix, per cent.
	Large	Small						
Silicon.....	0.58	0.54	0.98	0.58	0.52	0.86	0.48	0.85
Phosphorus	1.82	2.38	0.29	1.44	0.66	0.30	1.65	0.40
Manganese.	1.17	1.22	0.72	1.02	0.78	0.70	2.25	1.92

Because of their high phosphorus content, the globules have a much lower melting point than the matrix. When the matrix solidifies, the still-liquid alloy (phosphide eutectic) is pressed into the contraction cavities where it hardens in the shape of spherical masses.

3. Crystal Formation in Cavities.—The pigs of low-spiegel, puddle iron with 5 to 7 per cent. manganese often contain internal cavities filled with well-developed, leaf-like crystals. When the pig is first broken these crystal leaves have a mirror surface, which on contact with the air soon becomes coated with a layer of oxide, brownish yellow to deep blue in color and so thin that it can be neglected as far as its effect on the analytical results is concerned. The chemical study of the crystals and the matrix always shows a marked difference in the composition of the two. Platz[3] made numerous studies of crystals of this kind with the corresponding matrix. His results were:

[1] B. Platz, Stahl u. Eisen, **1887,** 639.

[2] Convex elevations on the surface of the larger cavities.

[3] Platz, Stahl u. Eisen, **1886,** 244.

TABLE 6.—ANALYSES OF CRYSTALS AND MATRIX

	I		II		III	
	Crystal leaves per cent.	Matrix, per cent.	Crystal leaves per cent.	Matrix, per cent.	Crystal leaves per cent.	Matrix, per cent.
Silicon.....	0.26	0.39	0.22	0.52	0.10	0.31
Phosphorus...	0.17	0.52	0.38	0.59	0.27	0.56
Manganese....	6.57	6.12	6.97	6.01	6.38	5.87
Carbon.....	4.80	4.39	4.77	4.38	4.63	4.28

The crystals are always poorer in phosphorus and silicon and richer in manganese and carbon. Their composition is probably very close to that of the primary solid solution which first separates on cooling.

4. Separations on the Outer Surface of White Iron.—It is well-known that when molten white iron is allowed to stand, small masses of metal separate which are very different from the matrix in composition. Ledebur[1] found lumps weighing more than 500 g. in white pig iron which was rich in manganese and phosphorus (basic Bessemer pig).

TABLE 7.—ANALYSES OF THE MASSES SEPARATING ON THE SURFACE OF WHITE IRON

	Manganese	Sulfur
The lumps contained.....	up to 9 per cent.	up to 3 per cent.
The matrix contained.....	3 to 4 per cent.	0.3 per cent. at most

The lumps were composed, therefore, chiefly of manganese sulfide. They solidify while the matrix is still liquid.

With mottled and very hard pig iron, solid, leaf-like formations (called "bugs" by Ledebur) frequently separate on the surface of the molten metal. These vary in size up to 10 mm. diameter and are essentially oxidic compounds.

Ledebur[2] gives the composition of some of these "bugs."

[1] A. Ledebur, "Handbuch der Eisen- und Stahlgiesserei," 3rd edition, 1901, p. 38.

[2] *Loc. cit.*

TABLE 8.—ANALYSIS OF A "BUG"

	Per cent.
Silicic acid	29.30
Ferric oxide	13.46
Ferrous oxide	46.73
Manganous oxide	6.40
Phosphoric anhydride	2.66
Manganese sulfide	1.25

Platz[1] also studied many of these formations. Some of his analyses are given in the following table.

TABLE 9.—ANALYSES OF "BUGS"

	Very low grade white iron, per cent.	Low grade white iron, per cent.	Very low grade white iron, per cent.	Low grade white iron, per cent.	White puddle iron, per cent.
Silicic acid	4.12	11.84	4.92	11.16	8.49
Phosphoric acid	5.91	4.49	9.75	7.55	11.93
Manganous oxide	8.97	11.14	12.80	11.54	0.46
The corresponding matrix contained:					
Silicon	0.13	0.56	0.21	0.50	0.31
Phosphorus	0.408	0.41	0.75	0.77	2.03
Manganese	1.71	1.76	1.86	2.29	0.38

If these "bugs" happen to get into the mold when the pig is poured they may be partially reduced by the carbon in the iron. Small metallic globules are formed in this way that differ very materially in composition from the rest of the casting.

All of the phenomena described in paragraphs 2 *to* 4 *may have a marked influence on the analytical results unless great pains are taken in getting the sample.*

5. Effect of Remelting on the Chemical Composition of White Iron.—It would not be fair to base the composition of the original white iron on the composition of the casting made from it, as the iron changes its composition very materially when it is remelted.

The method of melting (crucible, open hearth, cupola furnace) has a marked influence on the final composition.

After three remeltings of white iron in graphite crucibles (3

[1] B. Platz, Stahl u. Eisen, **1887,** 639.

parts graphite to 3.25 parts clay) Müller[1] found the following changes in the chemical composition:

TABLE 10.—ANALYSES BY MÜLLER

	Carbon, per cent.	Silicon, per cent.	Manganese, per cent.
Before remelting	3.59	0.07	2.04
After first remelting	3.71	0.57	1.91
After second remelting	3.77	0.76	1.85
After third remelting	3.63	1.07	1.86

The original white iron showed after each remelting a strong separation of graphite with a simultaneous increase in silicon content and decrease in the manganese content. After four remeltings the white iron had been changed completely to gray iron. Unfortunately the corresponding graphite determinations were not carried out.

A sample of *spiegel* with about 12 per cent. manganese was melted in a graphite crucible and allowed to cool slowly in the furnace. After breaking, the lower half showed a brilliant white fracture while the upper half gave a dull gray fracture. Microscopic study and chemical analysis showed that in the upper half, *A*, a marked separation of graphite had occurred while the lower half, *B*, had remained white.

The total carbon content of *A* was increased and the manganese content was reduced throughout by about 2 per cent. (See Table 11.)

TABLE 11.—SPIEGELEISEN WITH 12 PER CENT. MANGANESE AFTER MELTING IN A GRAPHITE CRUCIBLE

	Lower half, *B*, per cent.	Upper half, *A*, per cent.
Total carbon	5.43	5.19
Graphite	0.31	1.80
Combined carbon	5.12	3.39
Manganese	9.77	9.61
Silicon	0.94	0.88

[1] Stahl u. Eisen, **1885**, 181.

Fig. 33 (magnified 350 diameters) shows the structure of the lower white half *B*. Fig. 34 (magnified 117 diameters) is taken from the upper gray half.

M = 350

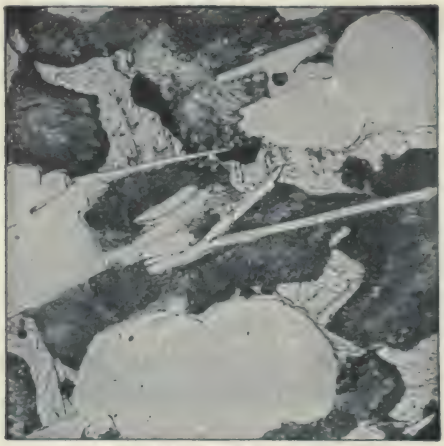


FIG. 33.—White spiegel.

M = 117

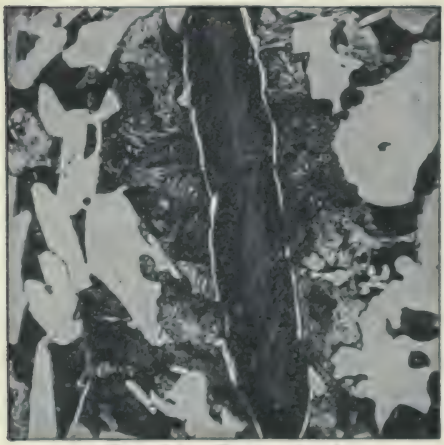


FIG. 34.—Gray spiegel.

Remelting in a reverberatory furnace also causes marked changes in the composition as is shown in the following analyses.[1]

[1] From H. v. Jüptner, "Grundzüge der Siderologie." Part 3, p. 375.

TABLE 12.—ANALYSES BY V. JÜPTNER

	I		II	
	Before	After	Before	After
	Remelting			
	Per cent.	Per cent.	Per cent.	Per cent.
Carbon	3.70	3.12	3.99	3.18
Silicon	0.135	0.021	0.205	0.025
Manganese	1.74	0.26	2.07	0.28
Phosphorus	0.103	0.036	0.075	0.056
Sulfur	0.057	0.032	0.058	0.034

The decrease in the amount of manganese and of silicon due to remelting is especially noticeable. The percentage of carbon, phosphorus and sulfur is also lowered.

When the remelting takes place in a cupola furnace, the chief effect is the oxidation of manganese. The silicon is protected from oxidation in this way. With a high manganese content (*Spiegel*) an increase in the silicon can occur, due to action on the furnace walls and on the slag. This is shown in the following table of analyses given by v. Köppen.[1]

TABLE 13

"Spiegel"	I		II		III		IV		V	
	Before	After	Before	After	Before	After	Before	After	Before	After
	Remelting									
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Carbon	3.98	4.13	4.40	4.62	4.48	4.60	4.62	4.96	3.63	3.67
Manganese	14.81	8.91	14.25	10.52	14.98	11.06	16.24	10.98	14.93	12.03
Silicon	0.14	0.50	0.12	0.49	0.12	0.42	0.40	0.66	0.33	0.41

The carbon content generally increases because of the intimate contact of the iron with the glowing coal. If coke is used for the smelting an increase in sulfur is often noticed.

6. Influence of the Rate of Cooling on the Composition of White Iron. Hard Castings.—Using the same iron it is possible

[1] E. v. Köppen, Dinglers polyt. Journal, **232**, 53.

to make a white or a gray casting, according to the way in which the piece is cooled. This fact is used in the manufacture of the

M = 1

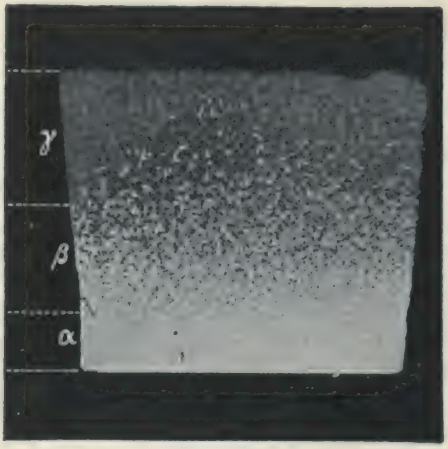


FIG. 35.—Hardened casting.

M = 350

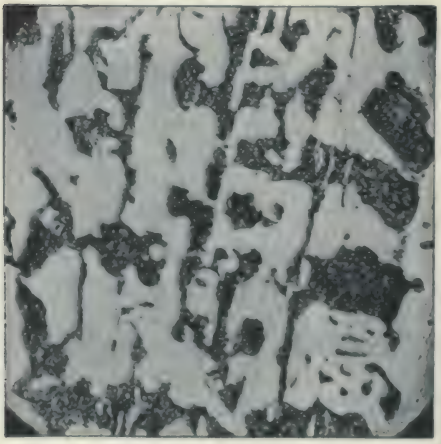


FIG. 36.—Section made from white border, α, in Fig. 35.

so-called *hardened castings* or castings which have been chilled purposely at certain points on the surface so that a more or less

thick layer of white iron forms (α in Fig. 35). The white, hard layer passes gradually into mottled iron (β in Fig. 35), while the core and the parts cooled slowly become gray (γ in Fig. 35). Metallographic examination will show the depth of the hard white layer.

Fig. 35 shows in natural size the gradual transition from white to gray iron.

Fig. 36 is a section from the white border, magnified 350 diameters. It is a mixture of cementite and pearlite.

Fig. 37 (magnified 350 diameters) shows the transition zone (mottled iron). In addition to the cementite and pearlite, small patches of graphite occur.

M = 350

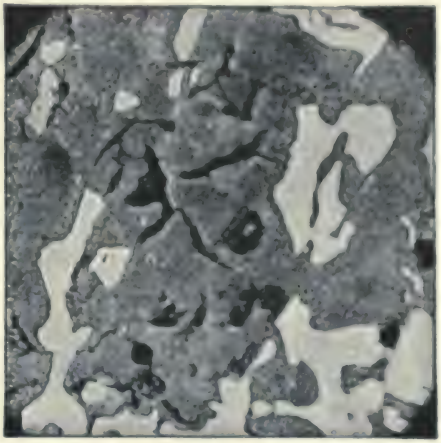


FIG. 37.—Section taken at the transition zone, β.

M = 350

FIG. 38.—Taken at the part γ.

Fig. 38 (magnified 350 diameters) corresponds to the gray part. Large plates of graphite are found in the pearlite. Cementite is present only in very small quantities.

An average analysis over the whole cross-section (α = white edge, β = transition zone of mottled iron and γ = gray iron core) would be of no value in this case. It may be useful, however, to know the composition of the individual layers,

α, β and γ. To get this, samples for analysis should be taken from each of the zones. After the depth of the layers has been determined by the microscope, shavings for analysis should be taken from the gray iron either by planing or boring and in the same way from the zone of mottled iron. The thin, white layer which is left and which cannot be machined is then broken to pieces.

Table 14 gives some analyses of various hard castings. Borings were taken from zone α (white iron) and zone γ (gray iron) only. The different specimens were cast in the usual pig molds, the bases of which were of iron and the walls of ordinary molding sand. The analyses were made by Wedding and Cremer.

TABLE 14.—ANALYSES BY WEDDING AND CREMER[1]

Sample number		Total carbon, per cent.	Graphite, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.	Copper, per cent.	Hardness, depth in mm.
1	white (α)	3.30	0.56	1.55	1.41	.....	.....	Trace	7–12
	gray (γ)	3.27	2.45	1.57	1.23	.....	.....	.....	
2	white (α)	2.87	0.14	1.64	1.39	0.68	0.03	.....	15–20
	gray (γ)	2.37	2.27	1.50	1.08	.....	0.03	Trace	
3	white (α)	3.12	0.09	1.16	1.33	0.51	0.04	Trace	20–28
	gray (γ)	3.07	2.43	1.22	0.87	0.49	0.039	.....	
4	white (α)	3.26	0.08	0.91	1.53	0.52	0.08	.....	32–48
	gray (γ)	3.05	1.86	1.09	1.16	0.56	0.08	.....	
5	white (α)	3.16	0.06	0.86	1.02	.....	.....	.....	36–50
	gray (γ)	2.53	1.56	0.82	0.82	0.82	.....	Trace	
6	white (α)	3.07	0.03	0.75	1.05	0.62	0.03	.....	55–75
	gray (γ)	2.42	1.52	0.70	1.01	0.59	0.03	.....	
7	white (α)	3.20	0.03	0.82	0.16	0.88	0.10	Trace	35–90
	gray (γ)	2.89	2.27	0.81	0.15	0.88	0.10	.....	

The total carbon and manganese are higher in all cases in zone α (white) than in zone γ (gray).

A large number of analyses of hard castings have been made by de Loisy.[2] Table 15 gives some of the results of his analyses. The specimens were hardened, cast rollers of French manufacture, all of which had given good service.

[1] H. Wedding and F. Cremer, Stahl u. Eisen, **1907**, 835.

[2] M. E. de Loisy, Revue de Metallurgie, "Memoires Tome II," p. 862.

TABLE 15.—ANALYSES BY DE LOISY

Firm	Roll No.	Sample taken from	Carbon			Silicon	Manganese	Sulfur	Phosphorus
			Combined, per cent.	Graphite, per cent.	Total, per cent.				
Perry & Co.	1	White part	2.10	0.45	2.55	0.68	0.38	0.15	0.50
		Gray part	1.22	1.20	2.42	0.70	0.39	0.17	0.47
Perry & Co.	2	White part	2.85	0.35	2.70	0.75	0.40	0.13	0.59
		Gray part	0.98	2.00	2.98	0.70	0.48	0.16	0.57
Perry & Co.	3	White part	1.90	0.68	2.58	0.91	0.40	0.16	0.50
		Gray part	1.14	1.75	2.89	0.89	0.38	0.18	0.46
Perry & Co.	4	White part	2.52	0.60	3.12	0.42	0.47	0.09	0.52
		Gray part	0.40	2.50	2.90	0.65	0.48	0.10	0.62
Le Creusot	5	White part	1.70	1.40	3.10	0.63	0.50	0.08	0.42
		Gray part	0.48	2.50	2.98	0.65	0.50	0.06	0.47
Le Creusot	6	White part	2.37	0.54	2.91	0.72	0.87	0.07	0.64
		Gray part	0.91	1.97	2.88	0.74	0.86	0.06	0.64
Le Creusot	7	White part	1.99	0.82	2.81	0.80	0.76	0.09	0.52
		Gray part	0.68	2.11	2.79	0.81	0.78	0.08	0.53
Le Creusot	8	White part	2.17	0.85	3.02	0.71	0.79	0.08	0.62
		Gray part	0.61	2.46	3.08	0.67	0.81	0.08	0.62
Le Creusot	9	White part	2.41	0.49	2.90	0.64	0.68	0.09	0.61
		Gray part	0.82	2.09	2.91	0.62	0.71	0.10	0.60

With the exception of rolls 2, 3, 8, and 9 the analyses show an enrichment of the total carbon in the white (hard) layer.

The differences are still more strongly marked in the chilled castings analyzed by Ledebur[1] as shown in the following table.

TABLE 16

Material	Sample taken from	Total carbon, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.	Copper, per cent.
Chilled armor	White part	3.31	0.26	1.03	[2]	[2]	0.08
	Gray part	3.03	0.71	1.08	[2]	0.08	[2]
Chilled wheel	White part	3.27	0.91	1.64	[2]	0.03	[2]
	Gray part	3.06	1.01	1.01	[2]	0.03	[2]
Chilled roller	White part	3.08	0.88	0.21	0.83	0.12	0.06
	Gray part	2.40	0.86	0.24	0.87	0.14	0.07
Chilled roller	White part	3.20	0.83	0.15	0.88	0.10	0.03
	Gray part	2.84	0.80	0.16	0.88	0.10	0.04

[1] Ledebur, "Handbuch der Eisen und Stahlgiesserei," p. 33.

[2] Not determined.

The difference in total carbon content between the white and the gray part is noticeable in all these castings. Ledebur does not give the percentage of graphite. In the wheel, the manganese content is greater in the white part while in the armor the percentage of silicon in the gray part is considerably higher than in the white zone.

Davis[1] has described a curious chilled casting. He found in a casting that the outer surface was of gray iron while the core was made of white iron, a statement which is confirmed by the following analyses.

TABLE 17.—ANALYSES OF A CHILLED CASTING

	Analysis of the	
	Outer gray part, per cent.	Inner white part, per cent.
Silicon	2.61	3.16
Sulfur	0.106	0.102
Phosphorus	0.60	0.74
Manganese	0.36	0.19
Graphitic carbon	3.40 (much graphite)	0.25
Combined carbon		3.04

In addition to the striking distribution of the graphite,[2] the marked differences in the manganese and silicon content are noticeable. While the outer gray part is richer in manganese, the inner white zone is richer in silicon and phosphorus.

7. Influence of Heating on the Chemical Composition of White Iron. Annealing, Malleableizing.—If white pig iron is held for a long time at a temperature above 700° C. (annealed), a decomposition of the iron carbide (cementite) and of the carbon-rich

[1] George C. Davis, "The Iron Age," **78,** 937.

[2] This phenomenon, which is only partially understood, is now believed to be due to the pressure of the outer, already hard layer on the metal inside. Because of this pressure, the graphite separation on the interior of the casting is prevented by the inability of the metal to expand to the extent necessary to allow graphite to form. A casting, hard on the inside, can occur only in a high silicon iron.

Whether this explanation is correct or whether a *seeding out* action (due perhaps to the graphite of the mold) plays a part in the formation is still an open question.

solid solution (martensite) takes place. Carbon (temper carbon) and iron (ferrite) separate out.

This decomposition does not take place uniformly throughout the entire mass of the castings, but starts at individual centers and spreads out from them. In this process, the removal of the carbon (black heart) is not intended, but merely a change of the combined carbon into temper-carbon. To what extent the desired result is obtained can be shown much more quickly and surely by metallography than by chemical analysis. Fig. 39 shows the effect of heating a piece of white pig iron for 108 hr. in wood charcoal. Large masses of temper carbon are imbedded in the ferrite and in addition cementite and pearlite are present.

M = 365

FIG. 39.—Annealed malleable cast iron.

M = 1

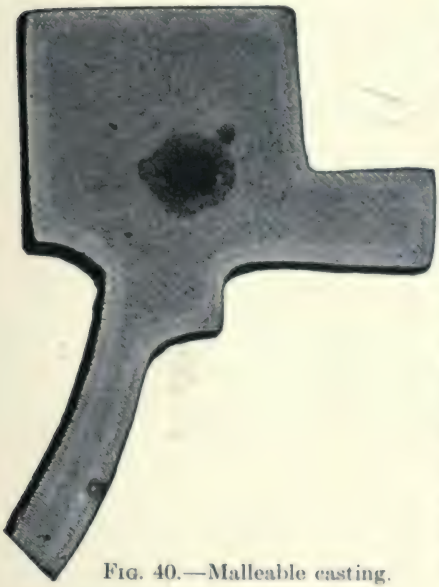


FIG. 40.—Malleable casting.

If the heating takes place in an atmosphere rich in oxygen (malleableizing), a simultaneous decarbonization takes place at the surface and gradually works in toward the center. Fig. 40 shows a casting treated in this way. It shows three distinct layers or zones with

varying carbon content: (*a*) a zone at the outside edges which is low in carbon (Fig. 41); (*b*) a transition zone richer in carbon

M = 200

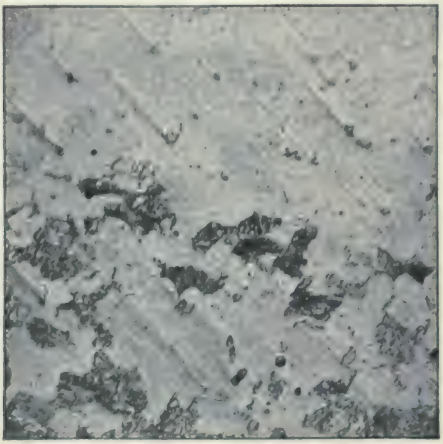


FIG. 41.

M = 200

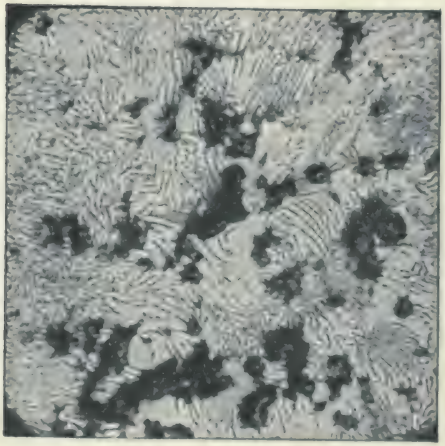


FIG. 42.—Central zone.

(Fig. 41); (*c*) a zone at the center where temper carbon has deposited (Fig. 42).

An average analysis is of no value in this case as it tells nothing of the way in which the carbon is distributed. It is best in all cases where an annealed piece is to be analyzed, to have the chemical analysis preceded by a metallographic examination. The chemical analysis of the malleable casting shown in Fig. 40 gave the following values:

TABLE 18.—ANALYSIS OF A MALLEABLE CASTING

	Samples for analysis taken from the core c. (See Figs. 40, 41, and 42.) Per cent.	Samples for analysis taken from the outer and from the transition zones[1] a and b. (See Figs. 40, 41 and 42.) Per cent.
Total carbon	3.48	1.45
Temper carbon	2.60	0.96
Combined carbon	0.88	0.49
Silicon	0.65	0.66
Manganese	0.04	0.04
Phosphorus	0.083	0.085
Sulfur	0.220	0.224
Copper	0.21	0.22
Nickel	0.05	0.05

Many analyses indicating the separation of temper carbon have been published. In addition to the length of heating and the temperature, the chemical composition also has its influence on the separation of temper carbon. Silicon favors while manganese hinders its formation.[2]

TABLE 19.—ANALYSES BY G. CHARPY AND L. GRENET

No.[3]	Carbon, per cent.	Silicon, per cent.	Manganese, per cent.	Sulfur, per cent.	Phosphorus, per cent.
1	3.60	0.07	0.03	0.01	traces
2	3.40	0.27	traces	0.02	0.02
3	3.25	0.80	traces	0.02	0.03
4	3.20	1.25	0.12	0.01	0.01
5	3.30	2.10	0.12	0.02	0.01

[1] The two outer zones were planed off and analyzed together. If the thin outer zone had been planed off and analyzed separately the differences would have been much greater.

[2] Stahl u. Eisen, **1902,** 813. *cf.* G. Charpy and L. Grenet, Bulletin de la société d'éncouragement pour l'industrie nationale, **1902,** 399.

[3] Samples 1 to 4 were originally free from graphite. Sample 5 had 0.2 per cent. graphite.

Five different kinds of white iron of the composition shown in Table 19 were heated for 4 hr. at different temperatures. The percentages of temper carbon and combined carbon after the heating were as follows:

TABLE 20.—ANALYSES BY G. CHARPY AND GRENET

No.	Heated 4 hr. at							
	1100°		1000°		900°		700°	
	Temper carbon	Combined carbon	Temper carbon	Combined carbon	Temper carbon	Combined carbon	Temper carbon	Combined carbon
1	1.15	1.74	1.03	1.74	.....	.....	1.87	0.43
2	1.26	1.93	1.00	1.62	.....	.....	.....	.....
3	1.61	1.26	1.60	1.52	1.67	1.17	2.56	0.38
4	2.10	1.02	2.20	0.98	2.32	0.90	.....	.....
5	2.18	1.00	2.10	0.93	2.33	0.90	2.67	0.28

In most of the samples there is a marked decrease in the total carbon. This means that in addition to the separation of temper carbon there is a decided combustion of the carbon especially noticeable on the surface of the sample. The core will, therefore, be considerably richer in carbon as is shown by the analyses. The above example illustrates the fact that in many cases the chemical analysis alone is not enough to explain the chemical changes taking place in the material.

The following analyses by Wüst[1] show very clearly the marked difference in carbon content between the edge and the center.

Two rods of white iron (10 mm. in diameter) were imbedded in iron oxide. Rod *X* was heated for 110 hr. at 940°, rod *VII* was heated for 24 hr. at 960°. The analyses were:

TABLE 21

Rod *X*			Rod *VII*		
	Edge, per cent.	Center, per cent.		Edge, per cent.	Center, per cent.
Total carbon.....	1.07	3.98	Total carbon.....	2.02	3.97
Temper carbon.....	0.21	3.86	Temper carbon.....	1.54	3.50
Combined carbon...	0.86	0.12	Combined carbon...	0.48	0.47

[1] F. Wüst, Metallurgie, **1908**, 9.

The original specimen contained 4.17 per cent. total carbon and only traces of graphite.

When the heating is done with coke or coal, the sulfur content usually increases because of the sulfur in the heating material. This increase takes place only in the outer layer. The percentages of manganese, silicon and phosphorus generally stay unchanged. The following analyses by Davenport[1] show the behavior very clearly.

TABLE 22

First experiment	Carbon	Silicon	Phosphorus	Manganese	Sulfur
Before heating	3.44	0.44	0.31	0.53	0.059
After one heat	1.51	0.44	0.32	0.58	0.067
After two heats	0.10	0.45	0.31	0.52	0.083
Second experiment:					
Before heating	3.48	0.58	0.28	0.58	0.10
After one heat	0.43	0.61	0.29	0.61	0.14
After two heats	0.10	0.61	0.29	0.57	0.16

The increase in sulfur content is easily recognized.

As average analyses are given in the table, the differences in sulfur content between the surface and the interior are not shown.

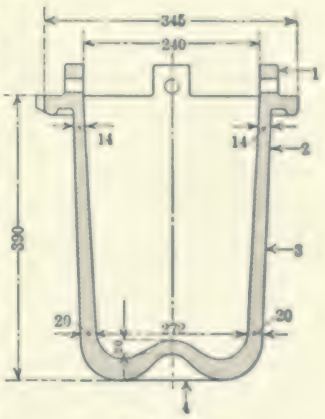


FIG. 43.

In the case of large pieces, if the heating temperature is not the same in all places or if the piece is not in good contact with the malleableizing agent (*e.g.*, ferric oxide) at all points, it may happen that some places are only partly malleableized or not malleableized at all. White, hard spots are left in the casting which become unpleasantly noticeable when the piece is machined or in later use. This condition is sometimes found in an incompletely annealed wheel. In one spot it may show the characteristics of white

[1] R. Davenport, Dinglers polyt. Journal, **207**, 51.

iron (see Fig. 10) while in all other parts of the casting there is plenty of temper carbon. (See Fig. 8.)

Tempering is often produced unintentionally. Wüst[1] describes an interesting case of this accidental annealing. A gas retort of white iron (Fig. 43) was exposed for a long time to the action of furnace gases. The samples taken at the points marked 1 to 4 gave the following values:

TABLE 23

	Samples taken at			
	1 Per cent.	2 Per cent.	3 Per cent.	4 Per cent.
Total carbon	3.39	3.33	3.04	0.50
Graphite and temper carbon	0.48	1.05	2.10	0.47
Combined carbon	2.91	2.28	0.94	0.03
Silicon	0.73	0.70	0.66	0.49
Manganese	0.48	0.46	0.44	0.39
Phosphorus	0.081	0.074	0.073	0.079
Sulfur	0.128	0.159	0.230	0.498
Oxygen	0.05	0.12	0.35	0.75

The shavings taken at 1 correspond to the original composition of the iron. A decided change in the chemical composition has been produced by the malleableizing effect of the flue gas. The greatest change has taken place at the bottom of the retort which was most directly exposed to the action of the hot gas. The total carbon grows less as the bottom is approached and the relative amount of temper carbon increases, the silicon content grows steadily smaller and there is an increase in both the sulfur and oxygen.

The effect of having an untrained workman take samples at random from the retort just described and sending them to different laboratories for a report on the composition of the retort material can be imagined. The result would be a series of analyses which would have no apparent connection with one another. Metallographic examination shows at once the reason for the varying results.

[1] F. Wüst, Stahl u. Eisen, **1903**, 1136.

CHAPTER VIII

GRAY CAST IRON

1. Sampling Gray Iron.—In this case, as in all others where a cutting tool can be used, the whole cross-section[1] should be planed down to get an average sample for analysis. Borings should not be used.

During the planing and collecting of the sample, the precautions mentioned in Chapter VI, p. 35, should all be observed or there is likely to be a large loss of graphite.

FIG. 44.

For the analysis of a single piece, a pig for example, approximately equal quantities of shavings should be taken from different places (marked 1, 2 and 3 in Fig. 44) and then combined to make an average sample.

Shavings from dark gray iron are never of equal size. On planing, a coarse part I and a finer part II are always formed.

The finer part II also contains the graphite plates torn out by the plane. If the shavings are shaken for a long time in a glass bottle, it is usually possible to separate a still finer part which is much richer in carbon than either of the other two. After the sample bottles have been filled with the shavings and allowed to stand for some time, the three grades of material separate of their own accord. The coarsest shavings stay at the top, the next coarser are below in the bottle, and at the bottom are found the finest particles which are rich in graphite.

Even if the contents of the bottle are thoroughly mixed, it is difficult to get a correct average sample for analysis. For exact work, as in an umpire analysis, it is always necessary in this case to divide the sample by sifting it into two or three portions, each part to have material of the same size. The weight of each portion is then taken and the final sample for analysis is prepared by mixing together some of each sample in the proper

[1] Exceptions to this rule will be mentioned later.

proportion by weight. The method is best shown by the following example.

The total weight of shavings made by the plane was 693 g. By means of sieves this material was subdivided into parts I, II and III

I coarse part = α grams (469 g.)
II middle size = β grams (193 g.)
III finest part = γ grams (31 g.)

To get a 1 g. sample the weighing should be as follows:

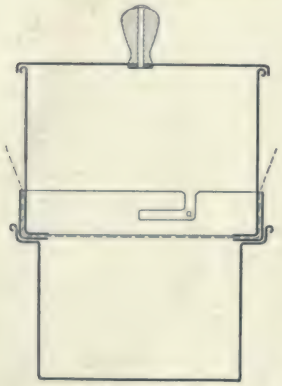


FIG. 45.

$$\text{Of I} = \frac{\alpha}{\alpha + \beta + \gamma} = 0.6768 \text{ g.}$$

$$\text{Of II} = \frac{\beta}{\alpha + \beta + \gamma} = 0.2785 \text{ g.}$$

$$\text{Of III} = \frac{\gamma}{\alpha + \beta + \gamma} = 0.0447 \text{ g.}$$

The three parts should then be combined to make a single sample.

The brass sieve shown in Fig. 45 is well adapted for this use. The upper cover must fit tightly in order to avoid any possible loss of the finest part as dust. Sieves with 80 and 120 meshes to the linear inch suffice for all analytical work.

How different the chemical composition of the different parts can be, especially in the percentage of total carbon and graphite, is shown by the following examples.

Example 1.—From a square bar (130 × 130 mm.) of dark gray cast iron, 189 g. were taken by planing over the entire cross-section.

After sifting through an 80-mesh sieve there were obtained:

173 g. of coarse I
16 g. of fine II[1]

[1] Part II showed a distinct tendency to separate on shaking. The shiny black graphite plates collected on the surface and were readily distinguished from the gray iron. A second, finer sieve ought to have been used in this case because the separate graphite determinations varied from 12.64 to 10.68, a deviation which could only be due to segregation.

The analyses are given in the following table:

TABLE 24.—DARK GRAY CAST IRON

	I In coarse part, per cent.	II In fine part, per cent.	Average composition of sample as calculated from I and II,[1] per cent.
Total carbon	2.62	11.66	3.39
Graphite	2.38	10.91	3.10
Combined carbon	0.24	0.75	0.29
Silicon	2.44	2.27	2.42
Phosphorus	0.51	0.56	0.515
Sulfur	0.08	0.073	0.079

Example 2.—The differences are even more clearly shown in this second case in which three parts were separated. Planing over the cross-section of a pig of Swedish gray iron gave 693 g. of shavings. After passing through an 80- and a 120-mesh sieve there were obtained:

I = 469 g. coarse particles
II = 193 g. medium particles
III = 31 g. fine particles

Analysis of the three parts gave:

TABLE 25.—DARK GRAY IRON

	I In coarse part, per cent.	II In medium part, per cent.	III In fine part, per cent.	Average composition of the pig as calculated from I, II and III, per cent.
Total carbon	3.53	4.04	22.0	4.50
Graphite	2.12	2.53	20.94	3.07
Combined carbon	1.41	1.51	1.06	1.43
Silicon	0.81	0.83	0.76	0.80
Phosphorus	0.051	0.044	0.030	0.048
Sulfur	0.017	0.014	0.013	0.016

[1] The method of calculation is:

$$\frac{a\mathrm{I} + b\mathrm{II}}{\mathrm{I} + \mathrm{II}}$$

where a is the per cent. found in part I and b the per cent. found in part II. For the calculation, then, of total carbon in the table, the method is

$$\frac{2.62 \times 173 + 11.66 \times 16}{189} = 3.39 \text{ per cent.}$$

The differences in the graphite and total carbon content are considerably greater in this case than in the former one.

Finally the total carbon and graphite were determined in a 1 g. sample (taken with reference to the weight of the separate parts as explained on p. 60). The values found were:

Total carbon	4.43 per cent.
Graphite	3.03 per cent.
Calculated combined carbon	1.40 per cent.

These values agree well with the results calculated in Table 25. These studies show that in working with iron which is rich in graphite, the analyst must take every possible precaution not only in taking the sample but also in the final weighing; otherwise incorrect results are likely to be obtained.

2. Inequalities in the Chemical Composition of Gray Iron, Etc.—If the shavings to be used for the average analysis are taken from a single place instead of from the whole cross-section, the inequalities in the composition of the casting have an effect upon results obtained by analysis. Sampling by boring is also unsatisfactory if an accurate average analysis is to be made, as with inhomogeneous material the sample can be affected materially by the depth of the boring. The following example will show that very considerable differences in composition may exist between different points on the cross-section.

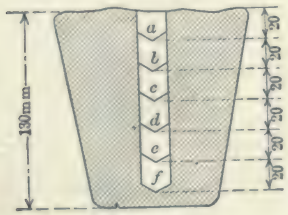


FIG. 46.

Borings were taken from a pig of basic Bessemer iron at points 20 mm. apart as shown in Fig. 46. Determinations of manganese and phosphorus in the borings gave the values shown in Table 26.[1]

The percentage of manganese and of phosphorus is different at each point on the surface of the pig.

Three pigs I, II and III were taken, the first from one end of the bed, the second from the middle and the third from the other end of the bed. Three samples were taken from each pig,

[1] From C. Reinhardt, Repertorium d. anal. Chem., **49**, 744.

TABLE 26

Sample taken at	Manganese	Phosphorus
a	3.42	2.91
b	3.11	2.41
c	3.22	2.65
d	3.11	2.58
e	3.06	2.39
f	3.17	2.65

at the points marked *O*, *M* and *U* in Fig. 47. Tabary[1] found the percentages of total carbon as follows:

TABLE 27

Borings taken at	Total carbon in pig		
	I Per cent.	II Per cent.	III Per cent.
O—top	3.53	3.55	3.44
M—center	3.55	3.72	3.55
U—bottom	3.01	3.44	3.40

The percentage of carbon is greatest in the center and least at the bottom of the pig.

A pig of dark gray iron from Bilbao studied by Ledebur,[2] was quite different in its composition. It contained less total carbon in the core than outside, and in the center where the graphite formation is generally greatest, there was less carbon than in the outer layer. The core was fine-grained and light, while the edge was coarse-grained and dark gray. Table 28 gives the analytical data. Graphite determinations were not made.

FIG. 47.

[1] P. Tabary, Stahl u. Eisen, **1894**, 1075.

[2] A. Ledebur, "Handbuch der Eisen- und Stahlgiesserei." Leipzig, 1901, p. 33.

TABLE 28.—ANALYSIS BY LEDEBUR

Fracture		Total carbon	Silicon	Manganese	Phosphorus	Sulfur
Outside	coarse-grained dark gray	3.87	3.65	1.58	0.02	0.03
Inside	fine-grained light gray	3.41	3.68	1.32	0.01	0.02

Adämmer[1] studied a hematite pig and found:

TABLE 29

	Total carbon	Silicon	Manganese	Phosphorus	Sulfur
Top	3.86	1.74	1.01	0.033	0.116
Bottom	3.71	1.74	0.99	0.031	0.081

Carbon and sulfur are higher at the top of the pig.

If differences of such magnitude occur in the cross-section of a piece with so small an area as a pig, it is easy to see how great the differences can be in a large casting. That this is really the case has been shown by numerous analyses.

Two tables showing analyses made by Adämmer on large castings will be given:

The first case was a steam chest weighing 8000 lb., of which the walls were from $\frac{7}{8}$ to 1 in. thick, $1\frac{3}{4}$ in. thick in the bore and $2\frac{3}{8}$ in. thick at the flanges. The cylinder was cast without discarding the head. The chemical composition was:

TABLE 30

	Total carbon	Silicon	Manganese	Phosphorus	Sulfur
In the ladle	3.59	1.31	0.86	0.37	0.072
Upper flange	3.53	1.45	0.73	0.46	0.144
Lower flange	3.29	1.22	0.65	0.36	0.101

The percentage of all constituents is higher in the upper flange than in the lower one.

The second case was a hollow beam weighing about 15,400 lb.

[1] H. Adämmer, Stahl u. Eisen, **22**, 898.

and having walls 5/8 in. thick. The casting was made from the top of the beam. Analysis gave:

TABLE 31.—ANALYSES BY ADAMMER

	Total carbon	Silicon	Manganese	Phosphorus	Sulfur
Top	3.46	0.63	3.02	0.55	0.192
Center	3.39	0.63	3.05	0.46	0.142
Bottom	3.41	0.63	3.08	0.46	0.080

The most marked differences are in the sulfur content.

That sulfur always has the tendency to rise to the top of the casting is shown clearly in the following analyses furnished by F. Wüst.[1]

The castings all had the same cylindrical form and weighed about 11,000 lb. The castings were made upright from a cupola furnace without a fore-hearth by means of a large ladle. Carbon and graphite were not determined and nothing is stated with regard to the method of taking the sample.

TABLE 32.—ANALYSES BY WÜST

Casting	Place from which the sample was taken	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.
1	Top	1.71	0.68	0.480	0.112
	Center	1.72	0.65	0.467	0.110
	Bottom	1.71	0.65	0.475	0.077
2	Top	1.49	0.69	0.422	0.212
	Center	1.47	0.68	0.421	0.208
	Bottom	1.49	0.54	0.435	0.111
3	Top	1.44	0.50	0.437	0.094
	Center	1.42	0.51	0.455	0.086
	Bottom	1.43	0.50	0.437	0.078
4	Top	0.96	0.76	0.439	0.210
	Center	0.96	0.71	0.450	0.174
	Bottom	0.97	0.57	0.464	0.100
5	Top	1.07	0.59	0.408	0.094
	Center	1.07	0.59	0.412	0.095
	Bottom	1.08	0.57	0.419	0.079

[1] F. Wüst, Stahl u. Eisen, **1903**, 1077.

TABLE 32.—ANALYSIS BY WÜST.—(*Continued*)

Casting	Place from which the sample was taken	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.
6	Top	0.99	0.71	0.56	0.110
	Center	0.97	0.71	0.48	0.117
	Bottom	1.17	0.71	0.49	0.099
7	Top	1.40	0.74	0.47	0.121
	Center	1.33	0.82	0.58	0.115
	Bottom	1.24	0.71	0.48	0.108
8	Top	1.02	0.53	0.411	0.108
	Center	1.00	0.52	0.411	0.112
	Bottom	1.04	0.53	0.419	0.104
9	Top	1.51	0.99	0.535	0.295
	Center	1.51	1.01	0.545	0.311
	Bottom	1.51	0.86	0.571	0.175
10	Top	1.51	0.79	0.579	0.210
	Center	1.46	0.89	0.535	0.304
	Bottom	1.43	0.73	0.569	0.162

Thomas D. West[1] calls special attention to the increase in sulfur in the upper part of large castings. In four castings he found:

TABLE 33.

	I Sulfur, per cent.	II Sulfur, per cent.	III Sulfur, per cent.	IV Sulfur, per cent.
Top of casting.....	0.117	0.115	0.084	0.055
Bottom of casting.....	0.083	0.094	0.070	0.047

Analyses were made of four wheels of gray iron, two samples being taken in each case, one from the center of the hub and the second from the rim. The results were as follows:[2]

Carbon and sulfur were not determined. The differences between the hub and the rim are particularly noticeable in the silicon content. Some of the differences in the results on phosphorus are also outside the limits of analytical error.

[1] Thomas D. West, "Metallurgy of Cast Iron," 1907.

[2] A. Martens, Stahl u. Eisen, **1894**, 797.

TABLE 34.—ANALYSES BY MARTENS

Wheel	Silicon		Phosphorus		Manganese	
	Hub, per cent.	Rim, per cent.	Hub, per cent.	Rim, per cent.	Hub, per cent.	Rim, per cent.
A	0.72	0.58	0.284	0.265	0.23	0.21
B	0.67	0.62	0.301	0.287	0.24	0.21
C	0.65	0.52	0.367	0.360	0.24	0.21
D	0.48	0.45	0.266	0.250	0.33	0.32

The examples given above show that the taking of representative samples from pigs or small castings can be done only by planing over the entire cross-section (or longitudinal section) and that the method of taking samples by boring at one place is not satisfactory because the chemical composition can differ so materially in different parts of a small specimen.

With large castings, where the taking of samples from the entire cross-section is impossible, or where the borings must be taken at some special place, the analysis should not be reported as an average value. The analyst should always show by a sketch where and how (planing, boring, etc.), the sample was taken. This precaution is absolutely necessary in control or umpire analyses and its neglect may cause much unnecessary misunderstanding.

3. Segregation Phenomena in Molten Cast Iron.—If a definite chemical composition is prescribed for a large casting and an average analysis is required, it is best to take samples during the casting, at the beginning, in the middle and at the end of the pour.[1] The taking of a single sample out of the molten metal is not satisfactory as there is a certain amount of segregation even in molten iron. Samples are taken in the usual way by planing the whole cross-section of each of the three pieces and the shavings combined to make the average sample.[2]

[1] At times it is better to take more frequent samples.

[2] The total carbon should be determined in this sample. The determination of graphite would be valueless, as the amount of graphite separating in a large casting is quite different from that in a small sample from the same melt.

TABLE 35.—ANALYSES BY WÜST

Sample No.	Total carbon, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.
1	3.59	2.00	0.65	0.88	0.080
2	3.56	1.98	0.62	0.88	0.078
3	3.47	2.01	0.65	0.88	0.085
4	3.53	1.93	0.68	0.84	0.081
5	3.51	2.03	0.65	0.88	0.083
6	3.56	2.01	0.70	0.88	0.085
7	3.67	1.90	0.68	0.73	0.080
8	3.53	1.90	0.70	0.64	0.088
Average	3.56	1.97	0.67	0.83	0.083
Greatest deviation from average	0.11	0.07	0.05	0.19	0.005
In per cent.	3.1	3.6	7.1	24.1	6.0

TABLE 36.—ANALYSES BY WÜST

Sample No.	Total carbon, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.
1	3.11	2.26	0.58	1.168	0.121
2	3.16	2.27	0.60	1.188	0.123
3	3.19	2.24	0.65	1.203	0.124
4	3.19	2.25	0.68	1.206	0.122
5	3.16	2.27	0.58	1.207	0.123
6	3.24	2.25	0.62	1.187	0.123
7	3.13	2.27	0.62	1.203	0.124
8	3.12	2.25	0.63	1.197	0.122
9	3.13	2.27	0.63	1.218	0.120
10	3.15	2.24	0.59	1.206	0.110
11	3.19	2.24	0.63	1.185	0.115
12	3.10	2.23	0.61	1.179	0.114
13	3.18	2.27	0.66	1.129	0.113
14	3.13	2.20	0.64	1.163	0.118
15	3.12	2.24	0.57	1.176	0.120
Mean	3.16	2.25	0.62	1.188	0.119
Average deviation from mean.	0.08	0.05	0.05	0.025	0.009
In per cent.	2.5	2.2	8.1	2.1	7.6

Values are found in this way that come very close to the true average percentages as the following analyses show.[1]

Example 1.—6500 lb. of iron were collected in the forehearth and while this was running into the ladle, samples were taken at intervals of about 1 min. These analyzed as shown in Table 35.

Carbon, silicon, manganese and sulfur show but slight variations. The phosphorus content of samples 7 and 8 is quite different from that of the other samples.

Example 2.—Casting and sampling as before.

The deviations are smaller here than in the first case but nevertheless show the tendency of cast iron in the liquid form to separate into layers.

With regard to the formation of layers in the ladle, Adämmer[2] writes as follows:

"During the casting of hard cast tubes it happened frequently that the castings were of different hardness. The first tubes were too soft, the middle set were good and the last lot much too hard, although all were cast from the same ladle."

Analysis gave the following values:

TABLE 37

	Total carbon, per cent.	Graphite, per cent.	Comb. carbon, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.
First iron from ladle (first tube)	3.82	3.0	0.82	0.85	0.84	0.09	0.130
Last iron from ladle (final tube)	3.61	2.32	1.29	0.66	0.73	0.07	0.098

A segregation in the case of total carbon, silicon, manganese and sulfur, which can have taken place only in the molten condition, is unmistakable here. The great differences in the graphite content might also be due to the difference in the temperature of the bath at the beginning and end of the pour.

4. Formation of Globules and Nodules.—Globules and nodules occur in gray iron exactly as they do in white iron and with a

[1] F. Wüst, Stahl u. Eisen, **1903,** 1077.

[2] H. Adämmer, Stahl u. Eisen, **1910,** 898.

composition quite different from that of the matrix. If this fact is not remembered in preparing the sample for analysis, results may be obtained which differ widely without any apparent reason. Ledebur[1] studied many of these formations inclosed in the matrix. His results are shown in the table.

TABLE 38

Iron	Sample taken from	Total carbon	Silicon	Manganese	Phosphorus	Sulfur	Copper	Arsenic	Titanium
Dark gray pig iron	Matrix	3.76	3.14	0.85	0.88	0.01	0.06	0.06	0.12
	Nodules	2.86	3.15	0.93	0.82	0.02	0.05	0.13	0.16
Dark gray pig iron from Westphalia	Matrix	3.45	3.28	1.03	0.96	0.01	[2]	[2]	0.08
	Nodules	2.67	3.18	1.05	1.27	0.01	[2]	[2]	0.10
Gray foundry iron	Matrix	3.79	2.52	0.57	0.58	[2]	[2]	[2]	[2]
	Nodules	3.11	2.22	0.70	1.25	[2]	[2]	[2]	[2]

Platz[3] gives the following analyses of globules in pig iron and in castings:

TABLE 39

Iron	Sample taken from	Silicon	Phosphorus	Manganese
Foundry iron No. 4	Matrix	1.16	0.29	0.78
	Large and small globules taken at random	0.63	2.37	1.36
	Large globules	0.68	2.03	1.27
	Small globules (from the same cavity)	0.62	3.30	1.48
Luxemburg foundry iron No. 5	Matrix	1.92	2.05	0.54
	Large globules	0.86	4.06	0.79
	Small globules	0.80	6.07	0.85
Casting	Matrix	1.21	0.33	0.73
	Globules	0.92	1.44	0.90
Casting	Matrix	1.12	0.53	0.71
	Globules	0.88	1.62	0.87

[1] Ledebur "Handbuch der Eisen- und Stahlgiesserei," 1901, p. 34.

[2] Not determined.

[3] B. Platz, Stahl u. Eisen, **1887**, 639.

These liquated globules sometimes occur on the surface of castings and vary in size from that of flax seed to pea size. The composition is in all cases very different from that of the matrix.

A study of these formations found on the surface of a cast plate was made by Ledebur[1] and the following values were found:

TABLE 40

	Matrix (cast plate)	Liquated globules
Total carbon	3.41	3.07
Silicon	2.04	1.63
Manganese	0.43	0.42
Phosphorus	0.44	1.98
Sulfur	0.08	0.05
Copper	0.03	0.01

As in the case of white iron, the globules formed on or in gray iron are very high in phosphorus.

In the analyses by Platz (Table 39) the manganese content was also higher while silicon was lower than in the matrix.

5. The Formation of Crystals and of Excrescences in Gray Iron.—A pig from a charcoal blast-furnace showed a large swelling that was completely filled with pine-tree crystals. The crystals were covered with a white coating. The chemical analysis of the matrix, the crystals and the white coating gave the following values:

TABLE 41.—ANALYSES BY LEDEBUR

	Matrix	Crystals	Coating
Total carbon	3.11	3.28	Practically pure silica
Silicon	1.85	2.05	
Sulphur	0.04	0.05	
Phosphorus	Trace	Trace	
Manganese	0.17	0.09	

In depressions on the sides of the pig, never on the top surface but always where the pig was in contact with the sand mold,

[1] Ledebur, "Handbuch der Eisen- und Stahlgiesserei," p. 36.

mossy or asbestos-like growths of a yellowish-white color are sometimes found. The analysis of the matrix and of the excrescences is given by Ledebur[1] as follows:

TABLE 42

	Matrix, per cent.	Excrescence, per cent.	
Total carbon	3.31	Silica	75.95
Silicon	3.27	Titanic acid	1.12
Titanium	0.03	Potassium oxide	1.80
Manganese	0.44		
Sulfur	0.02		
Phosphorus	1.13		

Ledebur assumes, as a possible reason for the formation of these excrescences, the existence of a volatile silicon compound, probably silicon sulfide, in pig iron. As soon as this compound comes in contact with the air, the sulfur burns to sulfurous acid and the silicon forms silicic acid which deposits on the colder walls of the pig or in the cavities.

6. Separations on the Surface of Gray Iron.—The formation of "bugs" when molten white iron is allowed to stand in the ladle (see p. 43) frequently occurs with gray iron.

TABLE 43.—ANALYSES BY PLATZ

Composition of the "Bugs"

	Foundry iron No. 1, per cent.	Foundry iron No. 3, per cent.	Gray puddle iron, per cent.	Fine grained gray iron with white rim, per cent.	Mottled iron, per cent.
Silicic anhydride	32.43	31.67	29.42	23.28	20.46
Phosphoric anhydride	0.39	0.64	1.36	2.02	2.32
Manganous oxide	13.01	11.91	11.23	9.61	8.97
The corresponding matrix contained					
Silicon	1.67	1.41	1.16	0.98	0.86
Phosphorus	0.28	0.282	0.29	0.289	0.295
Manganese	0.96	0.91	0.78	0.72	0.70

The composition of the "bugs" is quite different from that of

[1] A. Ledebur, Stahl u. Eisen, **1900.** 582.

the corresponding matrix, as the analyses by Platz,[1] given in Table 43, show.

7. Influence of the Rate of Cooling on the Amount and Kind of Graphite in Cast Iron.—The irregularities in composition which have just been described are due to layer formation or to segregation in the molten condition or during the cooling, but as in the case of white iron (p. 47) the amount and kind of graphite which separates in gray iron depends largely on the rate of cooling.

Small castings will show a lower graphite content and a different distribution of the graphite than large castings made from the same iron. Even at the same cross-section, when the total carbon is uniform throughout, the graphite content on the outer edge of the casting, where the cooling is most rapid, is often less than in the center.

FIG. 48.

Since the amount and kind of graphite determines in a large measure the mechanical properties of cast iron, it is often necessary to make analyses of different parts (edge, center, etc.).

Where the determination of graphite is the principal purpose of the analysis, it is better not to take the sample by planing or boring but to cut out small pieces (sections or cubes) as shown in Fig. 48. In this way the sources of error in sampling and weighing, described in detail on p. 59, are eliminated without complicating the analytical work in any way.

The following example[2] shows the effect of the nature of the cross-section on the graphite content.

It happens, also, particularly with bars of greater cross-section, that there is less separation of graphite at the corners because of the quicker cooling there.

Bars of various sizes ($\frac{7}{16}$ in. × $\frac{7}{16}$ in. to 6 in. × 6 in.) were cast in one piece as shown in Fig. 49. The average composition of the iron used was:

Total carbon	3.38 per cent.
Silicon	2.51 per cent.
Manganese	0.81 per cent.
Phosphorus	0.56 per cent.
Sulfur	0.095 per cent.

[1] B. Platz, Stahl u. Eisen, **1887,** 639.

[2] E. Heyn, Stahl u. Eisen, **1906,** 1295.

For the determination of graphite, samples were taken from the middle and from the edges as shown in Fig. 48. These samples were in the form of small pieces weighing about 2 g. each. The results are given in the following table and shown graphically in Fig. 50.

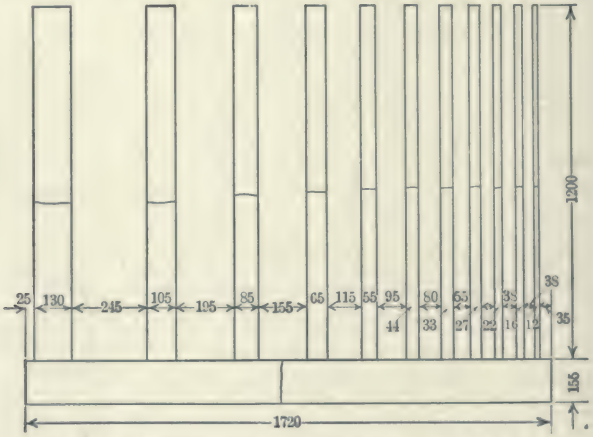


FIG. 49.—Dimensions in millimeters. Cf. Table 44.

TABLE 44.—ANALYSES BY E. HEYN

Cross-section in mm.	Center of bar		Corner of bar	
	Per cent. graphite[1]	Graphite in per cent. of total carbon	Per cent. graphite[1]	Graphite, per cent. of, in total carbon
155 × 155 (6″ × 6″)	3.00	88.75	2.68	79.3
130 × 130 (5¼″ × 5¼″)	3.00	88.75	2.68	79.3
105 × 105 (4¼″ × 4¼″)	2.97	87 9	2.92	86.4
85 × 85 (3⅜″ × 3⅜″)	3.06	90.5	2.95	87.2
65 × 65 (2⅝″ × 2⅝″)	3.03	89.7	2.85	84.5
55 × 55 (2 1/16′ × 2 1/16″)	2.98	88.2	2 94	86.9
44 × 44 (1¾″ × 1¾″)	2.84	84.0	2.78	82.2
33 × 33 (1 5/16″ × 1 5/16″)	2.77	82.0	2.62	77.5
27 × 27 (1 1/16″ × 1 1/16″)	2.66	78.7	2.55	75.5
22 × 22 (⅞″ × ⅞″)	2.55	75.5	2.55	75.5
16 × 16 (⅝″ × ⅝″)	2.55	75.5	2.53	74.8
12 × 12 (7/16″ × 7/16″)	2 50	74.0	Sample from the whole cross-section.	

[1] The value given is in each case an average of from two to five separate determinations. Each determination was made on a new section.

Table 44 and Fig. 50 show that the graphite content is lowest in the center of the thinnest bars. It increases with increasing cross-section and until a maximum is reached at 2⅝ in. × 2⅝ in. Investigation seems to indicate that under the conditions of the experiment (casting temperature, cooling rate, and silicon con-

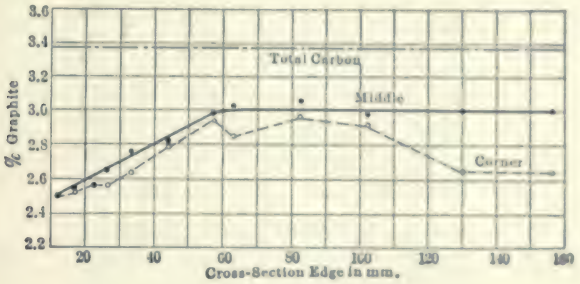


FIG. 50.

tent of the iron) the cross-section 2⅝ in. × 2⅝ in. is large enough to allow the maximum graphite separation in the core of the bar. At the corners of the larger bars, where the rate of cooling is considerably greater than in the center, the graphite content is much lower than in the center. With the small bars where the rate of cooling is approximately the same throughout, the differences in graphite content in different parts of the bar disappear.

That accidents also have considerable influence on the graphite separation at the corners of the bars is shown by the fairly wide variations in the analytical results.

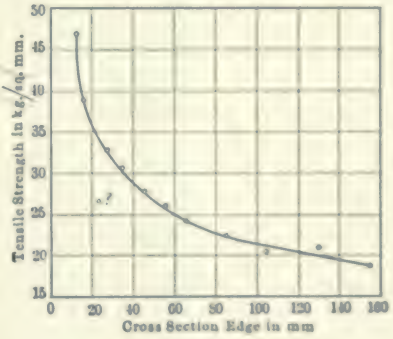
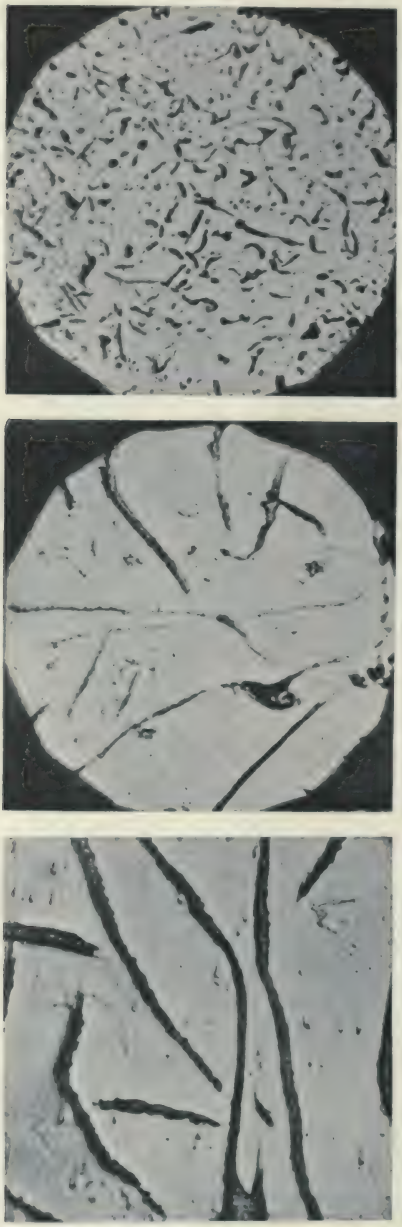


FIG. 51.

Not only the amount of graphite present but also the shape and size of the individual graphite plates may influence the physical properties of cast iron. Chemical analysis gives no indication of the size or shape of the graphite plates so that here again metallography must come to the aid of the chemist in explaining un-

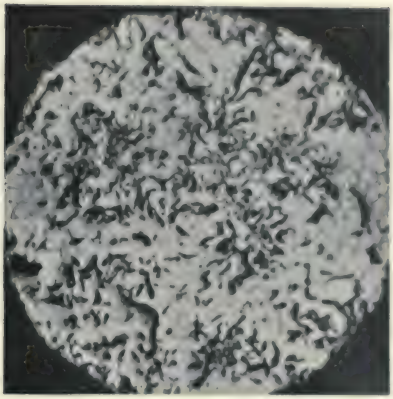


Rod $\frac{7}{16}''\times\frac{7}{16}''$

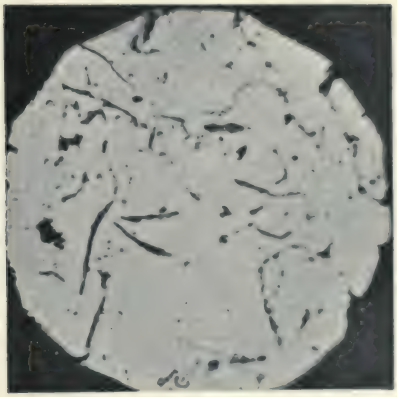
Rod $2\frac{5}{8}''\times 2\frac{5}{8}''$

Rod $6''\times 6''$

FIG. 52.—Influence of thickness



Rod $\frac{3}{16}$" × $\frac{3}{16}$"



Rod $\frac{5}{8}$" × $\frac{5}{8}$"

Rod 6" × 6"

on the separation of graphite.

usual conditions such as the differences in tensile strength of pieces of iron of identical chemical composition. The transverse strength of the bar shown in Fig. 49 is given in Fig. 51.

The transverse strength is greatest in the bar with the smallest cross-section. This decreases with increasing graphite content. In castings larger than $2\frac{5}{8}$ in. $\times$ $2\frac{5}{8}$ in. (the size at which the graphite content reaches its maximum and beyond which there is no change) there is a clearly marked decrease in the transverse strength with increasing size. Metallographic study explains these facts, as is shown in Fig. 52. The linear magnification is the same in all cases (117 diameters).

The photographs show very clearly that with increasing cross-section the size of the individual graphite crystals increases.

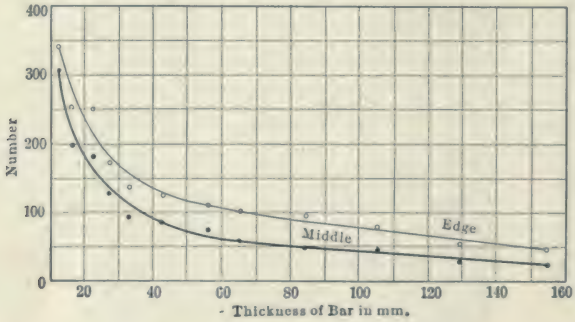


FIG. 53.

The difference between the bar with the largest cross-section and the bar with the smallest cross-section is very marked. It is, of course, obvious that graphite plates of the length and size found in the bar with the largest cross-section would break up the continuity of the iron and so tend to weaken the tensile strength.

If the number of graphite plates occurring in 1 sq. mm. of surface in each bar is determined and these numbers are plotted as ordinates and the thicknesses of the bars are used as abscissæ, the graphical results of the experiments described above are shown in Fig. 53. The number of graphite grains is greatest in the bars with the smallest cross-section and least in the largest ones. The number of graphite grains is greatest at the

edges and corners in spite of the fact that the total graphite content is smallest at these points. The individual graphite crystals must be smaller in size in the small rods and at the corners of the larger ones than at the center of the larger bars. The results obtained by counting the individual graphite plates is in complete agreement with the results obtained by the metallographic study.

The following example illustrates very clearly the influence of the size of the bar on the graphite content. It is taken from an investigation by Jüngst.[1] Seven round bars from $\frac{3}{16}$ in. to 2 in. in diameter, cast at the same time from a mixture with 1.93 per cent. silicon, 0.55 per cent. manganese, 0.712 per cent. phosphorus, and 0.090 per cent. sulfur gave the following values:

TABLE 45.—ANALYSES BY JÜNGST

Diameter of bar	2 in.	1½ in.	1⅛ in.	¾ in.	⅝ in.	⅜ in.	⅛ in.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Graphite.....	2.95	2.90	2.82	2.80	2.60	2.60	2.39
Combined carbon	0.42	0.50	0.60	0.60	0.72	0.78	0.99
Total carbon....	3.37	3.40	3.42	3.40	3.32	3.38	3.38

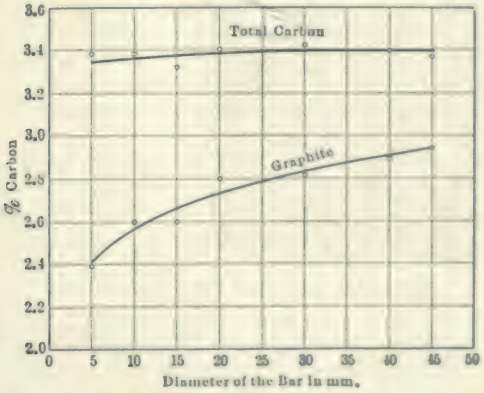


FIG. 54.

[1] Jüngst, Stahl u. Eisen, **1905**, p. 415.

The graphite content decreases regularly with increasing cross-section, the percentage of combined carbon increases and the percentage of total carbon stays about the same. (See also Fig. 54.) Jüngst's results do not show any marked differences in graphite content between the edges and the middle of the specimen. The arrangement, number and size of the graphite plates is markedly different at the edges and at the core of the specimens.

FIG. 55.

The following example[1] is also interesting as it shows clearly that, especially with gray iron, the chemical analysis alone often fails to explain unusual behavior.

Cast iron rich in silicon (the chemical composition is given below) was cast in a sand mold fitted with an iron bottom so that quenching experiments could be made. The mold was open at the top.

The fracture of the piece showed in the upper part (see Fig. 55) a very coarse grain with large graphite plates; the lower part of the specimen showed a sudden transition from the coarse to a fine structure in which the graphite plates were not visible. Chemical analysis of the upper and lower parts gave the following values:

[1] E. Heyn, Stahl u. Eisen, 1906, p. 1295.

TABLE 46.—GRAY CAST IRON

	In upper coarse-grained part, per cent.	In lower fine-grained part, per cent.
Total carbon	3.56	3.51
Graphite	3.42	3.41
Combined carbon	0.14	0.10
Phosphorus	0.09	0.09
Manganese	0.94	0.94
Silicon	3.30	3.31
Sulfur	0.058	0.058

The chemical composition is evidently the same in both parts but the structure is decidedly different. The upper part shows long and large graphite leaves (Fig. 56), while in the lower part the graphite is in a finely divided condition (Fig. 57). The graphite particles in the second case are arranged in the usual eutectic form and probably correspond to a true graphite eutectic. In spite of the same chemical composition of the two parts, the mechanical properties were quite different.

M = 350

FIG. 56.—Upper half.

8. Influence of Remelting on the Chemical Composition of Gray Iron.—Just as in the case of white iron (p. 44), it is found that with gray iron the chemical composition can be changed materially by remelting, the extent of the change depending on the way the remelting is done.

For this reason the analysis of the original material from which a casting is made may give only an approximate idea of the composition of the casting.

If a cupola furnace is used, the manganese is most readily

oxidized while the silicon, if the manganese is still high, will be affected but slightly. With high manganese content an increase in silicon may occur, due to the reduction of the slag.

M = 350

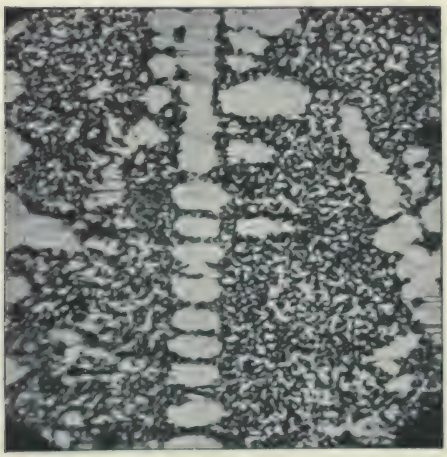


FIG. 57.—Lower half.

The silicon does not begin to burn until most of the manganese has been oxidized.

Carbon will stand a longer heating in the cupola furnace, where the iron is in immediate contact with the hot coke from which carbon can be taken as fast as it is used up, than in the reverberatory furnace where oxidation takes place quickly. With high manganese, the carbon content is likely to increase. Sulfur generally increases due to the presence of sulfur in the products of combustion, while the phosphorus content generally changes but little. These facts are illustrated by the following analyses taken from Ledebur's "Handbuch der Eisen- und Stahlgiesserei:"

TABLE 47.—ANALYSES BY LEDEBUR
(Remelting in a Cupola Furnace)

	Gray pig iron with high manganese		Gutehoffnung pig iron, No. 1		Coltness pig iron, No. 1		Gleiwitz pig iron	
	Before, per cent.	After, per cent.	Before, per cent.	After, per cent.	Before, per cent.	After, per cent.	Before, per cent.	After, per cent.
Total carbon	4.58	4.67	4.15	3.49	4.05	3.49	4.17	3.68
Silicon	2.27	2.44	2.05	1.55	2.52	2.07	1.52	1.33
Manganese	3.67	2.58	0.77	0.12	1.27	0.46	2.08	0.73
Copper	[1]	[1]	0.06	0.05	0.05	0.07	0.08	0.08
Phosphorus	[1]	[1]	0.61	0.72	0.72	0.87	0.33	0.47

[1] Not determined.

The influence of repeated remelting, especially the increase in sulfur, is shown in the following table.

TABLE 48.—ANALYSES BY LEDEBUR

Pig iron	Total carbon, per cent.	Graphite, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.
Before remelting..	3.10	2.35	2.30	2.00	0.29	0.06
After one melt....	3.33	2.73	2.42	1.09	0.31	0.04
After two melts...	3.32	2.57	2.29	0.80	0.32	0.05
After three melts..	3.30	2.48	1.92	0.66	0.27	0.05
After four melts...	3.34	2.54	1.38	0.44	0.30	0.10
After five melts...	3.31	2.16	1.30	0.45	0.30	0.09
After six melts....	3.34	2.08	1.16	0.36	0.28	0.20

9. Influence of Annealing on Gray Iron.—Long continued annealing in an atmosphere rich in oxygen can cause marked changes in the composition of gray cast iron, especially in the carbon content.[1]

Two gray iron castings were annealed at 1000° to 1050°, one of them seven times and the other eleven, after which analyses were made.

TABLE 49.—ANALYSES BY WÜST

	Casting 1		Casting 2	
	Original casting per cent.	After seven heats, per)cent	Original casting per cent.	After eleven heats, per(cent
Total carbon	3.66	0.10	3.74	0.28
Graphite	2.02	0.02	3.33	0.28
Silicon	1.58	1.70	1.59	1.45
Manganese	0.78	0.68	0.63	0.56
Phosphorus	0.267	0.368	0.089	0.062
Sulfur	0.157	0.781	0.090	0.315

The original gray iron, rich in carbon, has been changed into malleable iron. The high sulfur content after annealing is particularly striking. Unfortunately, Wüst does not state whether the increase in sulfur was chiefly on the surface or whether it extended into the casting.

[1] F. Wüst, Stahl u. Eisen, **1885**, p. 471.

Platz[1] has also given some analyses in his paper on "The Chemical Changes Caused by Annealing and Tempering Pig Iron."

According to Platz there occurs, in addition to the burning of the carbon, a segregation and slagging of the phosphorus. This is not at all impossible as the ternary eutectic (solid solution—carbide-phosphide) begins to melt at 950° C.

The above illustrations show that the sampling of castings for chemical analysis should always be preceded by a metallographical examination of the specimen to see whether or not it is homogeneous.

10. Disintegration of Cast Iron.—A phenomenon should be mentioned in this connection, the disregard of which may cause very serious analytical errors.

If castings, as, for example, water mains, lie for years in contact with moist earth a curious decomposition takes place. In some places the pipe, without losing its form, will change to a dull gray mass so soft that it can be cut with a knife. The reason for the change has not been satisfactorily explained. Moisture seems to be absolutely necessary. Whether the change is due chiefly to the oxygen content of the earth or to stray electric currents is still an open question.

M. Freund[2] analyzed some corroded water mains with the following results:

TABLE 50

	In original casting, per cent.	At the corroded spots, per cent.
Total carbon	2.5	8.10
Silicon	2.66	9.3
Phosphorus	1.9	6.5
Iron	[3]	46.18

Another soft mass obtained from a corroded water main contained:

[1] Stahl u. Eisen, **1885,** p. 471.

[2] M. Freund, Z. angew. Chem., **1904,** No. 2.

[3] Not determined.

TABLE 51.—CORRODED CAST IRON

	Per cent.[1]
Iron	49.4
Manganese	0.7
Phosphorus	5.3 = 12.15 phosphoric acid
Silicon	9.0 = 19.14 silicic acid
Carbon	8.5
Sulfur	0.37

The same sort of decomposition sometimes takes place with castings exposed to heat. For example, the outer surfaces of the cast iron coils of a hot water heater which had been exposed to the hot gases of the flame, showed places soft enough to be scraped off with a knife, especially at the threaded joints. The chemical composition of the soft material was as follows:

TABLE 52.—DECOMPOSED CAST IRON

	Per cent.
Total carbon	11.73
Graphite	9.77
Phosphorus	0.89
Sulfur (total)	1.28
Sulfur as sulfate	0.49
Silicon, chiefly as SiO_2	6.38
Iron, total (almost wholly combined with oxygen)	39.16
Manganese	0.75
Copper	0.16
Water (loss on drying at 120°)	9.13
Calcium, magnesium and aluminium	Traces
Oxygen and water of hydration	Remainder

These analyses indicate that the soft masses are decomposition products of cast iron. The decomposition may take place as a result of the action of furnace gases (sulfurous acid) and of moisture. The marked corrosion at the threaded joints was probably due to leakage of water at those points.

Thomas Steel[2] calls attention to a similar decomposition of economizer tubes. He found:

[1] The iron was present chiefly as oxide.

[2] Thomas Steel, J. Soc. Chem. Ind., **29**, 1141 (1910).

TABLE 53

	In unused pipe	In the uncorroded part of the used pipe
Graphite	2.76	2.41
Combined carbon	0.34	0.19
Phosphorus	1.25	1.28
Sulphur	0.11	0.09
Silicon	2.08	1.90

In the corroded part of the used pipe	Per cent.
Ferric oxide	37.86
Ferrous oxide	16.75
Graphite	8.69
Combined carbon	0.0
Phosphoric acid	9.48 = 4.14 phosphorus
Sulfur	0.0
Silicic acid	13.30 = 6.21 silicon
Moisture	13.34

M = 350

FIG. 58.—Decomposed cast iron.

It is noticeable that the graphite in a corroded casting is usually not a deep black but gray or grayish-white in color.[1]

[1] See O. Kröhnke, Metallurgie, **1910,** 674.

Fig. 58 shows a badly corroded gray cast iron magnified to 350 diameters. The graphite leaves appear light gray in contrast to the dark background.

Nothing more will be said of the possible sources of error in sampling pig iron or cast iron (white or gray). These sources are numerous and if the sampling is not done intelligently very serious mistakes can be made.

If the director of the laboratory cannot control the taking of the samples, he can be held responsible only for the correct analyses of the samples submitted and cannot guarantee that the analyses show what they ought to show. He cannot state that the results give the average composition of a pig or of a casting, that they show the disposition of the different constituents in a casting or whether corrosion or other harmful influence has had an effect on the material. Metallography is of the utmost importance and assistance in answering questions of this sort. Properly applied, it will protect the analyst from serious errors.

CHAPTER IX

INGOT IRON AND MILD STEEL

1. Taking an Average Sample from the Molten Charge.—If it is a question of getting a representative sample from a large heat, it is safest to prepare two test ingots about 12 to 18 lb. in weight, one at the beginning and one at the end of the pour. With a very large heat, a third sample taken at the middle of the pour is advisable. The small ingots are cut through the center lengthwise as shown in Fig. 59. Samples are obtained by planing over the surface indicated by a shaded line in Fig. 59. The shavings from the separate ingots are united to make a single average sample.

FIG. 59.

Under certain conditions it is better to analyze each ingot separately and take a mean of the results. It is possible to determine in this way whether or not segregation took place when the charge was in the molten condition, a thing which ought not to occur if the temperature is high enough.

Table 54 gives the analyses of a series of ingots taken from two different charges, *A* and *B*. The material was Siemens-Martin iron and four large ingots were cast from each heat.

TABLE 54.—ANALYSES OF TEST INGOT TAKEN DURING THE POURING OF THE HEAT

Heat	Sample taken at	Carbon, per cent.	Silicon, per cent.	Manganese, per cent.	Phosphorus, per cent.	Sulfur, per cent.	Copper, per cent.
A	Beginning of pour..	0.21	0.21	0.74	0.024	0.032	0.054
	End of pour.....	0.21	0.21	0.73	0.023	0.031	0.053
B	Beginning of pour..	0.34	0.26	0.78	0.026	0.034	0.055
	End of pour.....	0.34	0.25	0.78	0.025	0.035	0.054

In both cases the differences between the composition at the start and at the end of the pour are very slight, being within the limits of analytical error. Segregation in the molten state, therefore, has not taken place. The average of two analyses on each ingot would give a very representative value for the composition of the entire heat. It should be noted that these analyses do not give any information as to the distribution of the foreign substances in the ingot.

2. Chemical and Metallographical Study of the Solid Ingot.— If samples are not taken during the pouring as described in the preceding paragraph, it is not only difficult, expensive and time-consuming to get shavings from the ingot which really represent the composition of the original charge, but in the case of large ingots it is absolutely impossible.

Molten iron forms a solid solution (mixed crystals) with most of the foreign elements occurring with it. As regards the solidification of the solid solution, it may be said:

The solid solution, as it separates out, is always richer in the constituent with the highest melting point than is the melt with which the crystals are in equilibrium; or, in other words, the melt retains more of that constituent by means of which the solidification temperature was lowered than is present in the first crystals formed.

Now since the temperature at which pure iron solidifies (1505°) is lowered by all the impurities that occur in technical iron as well as by those elements which are added to it intentionally, it follows that when a large ingot solidifies, the solid solution that first separates on the cold walls of the mold is freer from those elements which caused the lower melting point (chiefly carbon, phosphorus, sulphur and manganese) than that part of the melt which cools more slowly. These foreign elements, therefore, are forced continuously toward that part of the casting which solidifies last. In the case of large ingots this point lies in the middle of the ingot near its head as indicated in Fig. 60. Segregation, therefore, takes place during the cooling.

For technical purposes it is often important to determine whether or not segregation has taken place in a mass of metal as only material which is practically free from segregation is suitable for certain purposes.

To determine by chemical means the extent to which segregation has taken place, an ingot may be cut lengthwise along the line *S–S* (Fig. 61) and borings taken at various points of the surface indicated in the drawing by cross-hatching. If the results of the analyses of samples taken from various places on the section are plotted (see Fig. 64) it is possible to get a fairly good idea of the distribution of the various constituents in the ingot. It must be remembered in this connection that these analyses give only the composition of a few selected points and that their average does not by any means represent the average composition of the ingot.

FIG. 60.

The diagrams shown in Figs. 62 and 63 were made in the way just described and the analyses at different points are shown in Table 54.

In spite of the low average content of phosphorus and sulfur, there is a marked segregation of the elements at the top of the ingot near the middle. Carbon and manganese are also richer in the top of the ingot while silicon and copper show no segregation. On the outside of the ingot the composition of the metal is about the same as at the top and bottom.

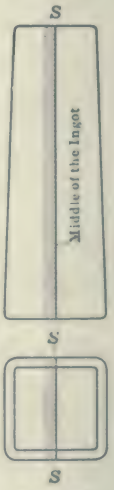


FIG. 61.

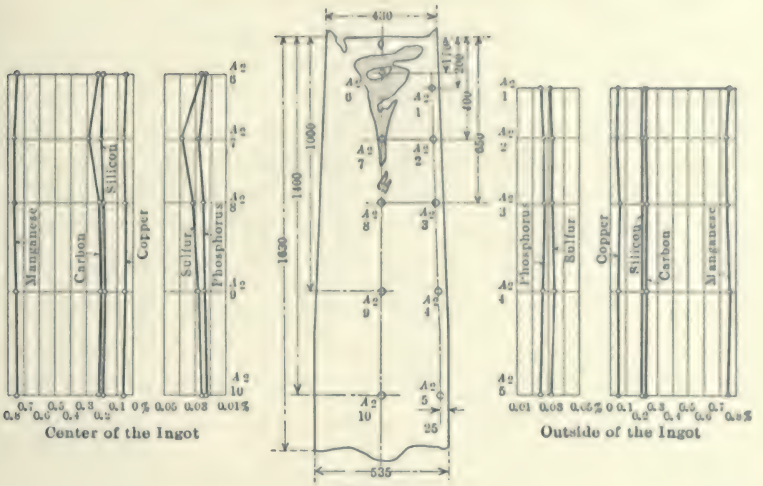
As a rule segregation takes place to a greater extent as the quantity of elements other than iron in the charge is increased. This is shown clearly in the following example.[1]

The average composition of an acid open-hearth steel (samples taken from the ladle) was 0.38 per cent. carbon, 0.052 per cent. phosphorus, 0.52 per cent. manganese and 0.061 per cent. sulfur.

The ingot showed marked segregation as illustrated in Fig. 64. (The analyses selected were from a section taken through the middle of the ingot.) The top of the ingot was particularly rich in phosphorus and sulfur and there was also a decided segregation of carbon.[2]

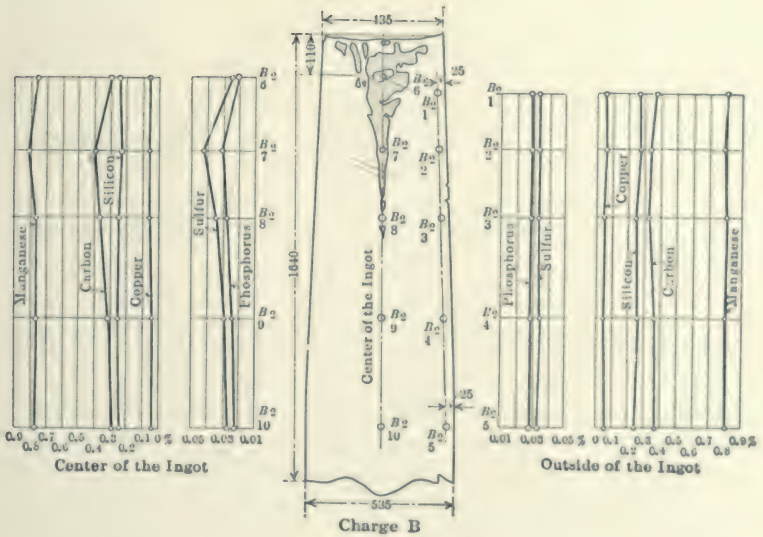
[1] Talbot, Iron and Steel Institute, 1905.

[2] For other examples of segregation in iron ingots see A. Martens, Stahl u. Eisen, **1894**, 797; F. Wüst and H. L. Felser, Metallurgie, **1910**, 363. A. Obholzer, Stahl u. Eisen, **1907**, 1155.



Charge A

FIG. 62.



Charge B

FIG. 63.

The question as to whether segregation exists or not is of the greatest practical importance, because the usefulness of the material for a definite purpose is often determined by the presence or absence of marked segregation.

The nearer together the points from which the borings are taken, the more definite the knowledge of the way in which the foreign elements are distributed. A purely chemical study like the one just described is very time-consuming and expensive

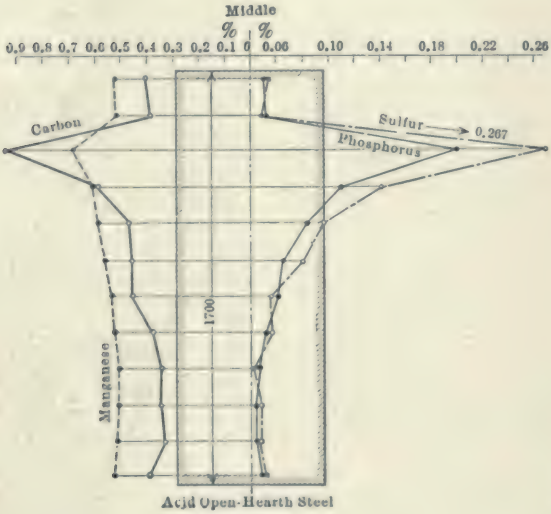


FIG. 64.

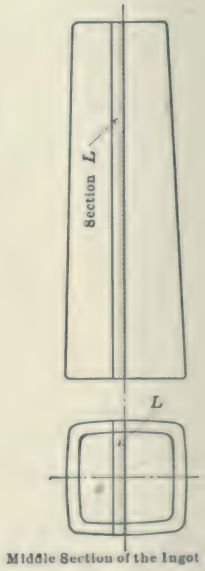


FIG. 65.

and, moreover, the ingot must be remelted as it is no longer suitable for rolling.

Under these conditions, the macroscopic study of the specimens has been very successful in detecting segregation in the material, particularly the segregation of phosphorus. (The section should be etched with copper ammonium chloride according to the method of E. Heyn.) (See p. 12.) The metallographic method shows clearly whether or not segregation has taken place, shows the boundaries of the zone of segregation and, to an ex-

perienced observer, gives an approximate knowledge of the extent to which segregation has taken place.

In studying large ingots, to determine possible zone-formation due to segregation, the best way is to cut out a section through the middle of the ingot as indicated in Fig. 65. The section is then ground and polished on the side indicated by the cross-hatching.[1] After the surface has been cleaned with alcohol, it is suspended as shown in Fig. 66 and dipped in a wooden trough (see Fig. 67) containing the etching reagent (copper ammonium chloride 1 : 12).

After etching for 2 or 3 min., the section is taken out, the copper deposit removed with running water and a piece of cotton, and the water rinsed off by pouring absolute alcohol over the surface of the metal.

The treatment is the same as with

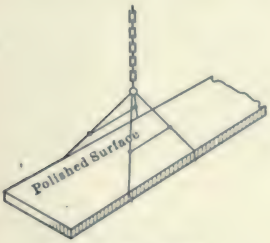


Fig. 66.

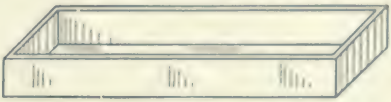


Fig. 67.

smaller specimens. (See Chapters II and III in this book.) Fig. 68 shows a section from a 3-ton ingot treated and etched as described above. There is no zone formation in this specimen; the material is nearly free from segregation.[2]

It is not always possible or necessary to cut out so large a sec-

[1] It is very difficult in working with so large a piece to get a surface entirely free from scratches. In preparing the specimen for treatment with copper ammonium chloride, to determine macroscopically the nature of the segregation, a less careful treatment of the specimen is required. The following procedure is satisfactory: First, plane the surface till smooth. Remove the marks of the planing tool with fairly coarse emery. Then polish with a wooden disk covered with leather which is sprinkled with very fine emery powder, and finish with a felt disk using rouge and oil. In cutting and polishing small sections hold the piece against the rotating disk. In polishing large sections, hold the plate still and move the rotating disk back and forth over its surface.

[2] The ingot was prepared by the Harmet process which accounts for the lack of segregation.

tion for grinding, polishing and etching. This cannot be done, for instance, if the ingot is to be rolled.

Fig. 68.—Etched section from a 3-ton ingot.

If in such a case it is desirable to get an approximate idea of the distribution of foreign elements in the ingot, it may be done, as indicated in Fig. 69, by taking a section at the top of the ingot, at *K*, equal to about one-fourth of the entire cross-section, a similar piece near the bottom, at *F*, where the segregation is least, and examining these specimens after polishing and etching.

Fig. 70 shows the pol-

Fig. 69.

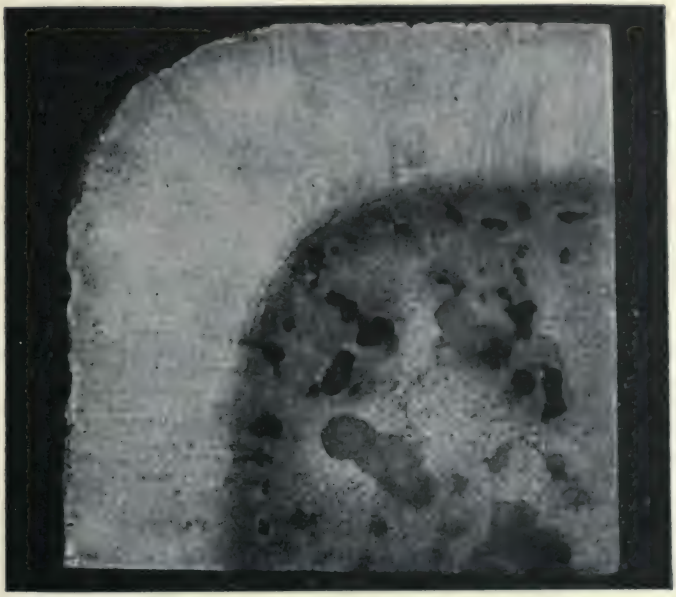


FIG. 70.—Section *K* from the top of the ingot.

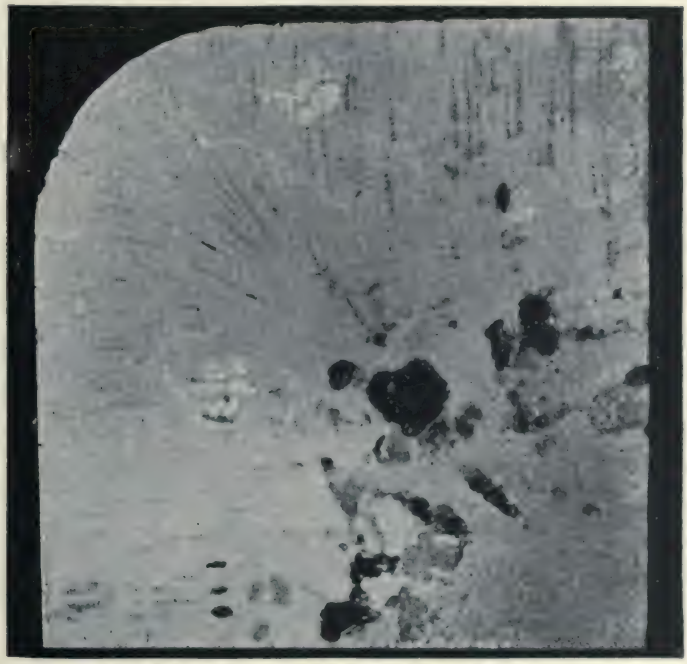


FIG. 71.—Section *F* from the base of the ingot.

ished section from the top of the ingot and Fig. 71 one from the bottom of an ingot of basic-Bessemer steel. The deepest black spots are due to blow holes.

A circle of large holes separates the inner from the outer zone in both sections. The core is darker in both cases than the outer edge. In this inner zone are found larger or smaller spots rich in phosphorus. A dark color after etching with copper ammonium chloride is generally an indication of a high phosphorus content (*cf.* p. 27). The other impurities, however, particularly the oxide and sulfide compounds, also tend to collect at those places where the phosphorus content is greatest, so that in case the color is unusually dark it is safe to assume that the sulfide and oxide content is also high.[1]

It will be noticed that at the top of the ingot the boundary between the inner and outer zones is sharply marked by a dark band, while at the lower end (Fig. 71) there is a gradual transition without any sharply marked, dividing line. The dark color in the inner zone of section, *F*, from the foot of the ingot, is very slight as compared to that of the corresponding part of the upper section, *K*. The conclusion may be drawn from these facts that there is a marked difference in the percentage of impurities at the top and at the bottom of the ingot. This opinion is confirmed by analyses made from different parts of the ingot.

TABLE 55

	From top of ingot		From bottom of ingot	
	Inside, per cent.	Outside, per cent.	Inside, per cent.	Outside, per cent.
Carbon	0.11	0.06	0.07	0.07
Manganese	0.52	0.48	0.47	0.46
Phosphorus	0.15	0.07	0.08	0.05

The macroscopic examination (etching test) gives, therefore, a satisfactory idea of the distribution of foreign matter in the material. It shows whether zone-formation due to segregation

[1] In case of doubt, microscopic examination and the sulfur print on silk will confirm or disprove the presence of these constituents.

has occurred, shows clearly the boundaries between the different zones, and gives a means of determining the most suitable places from which to take samples for chemical and mechanical tests.

3. Chemical and Metallographic Study of Rolled Steel.—Segregation in wrought iron and steel cannot be wholly overcome.

FIG. 72.—From the top of the ingot.

FIG. 73.—From the base of the ingot.

With suitable precautions, it is possible to reduce it to a certain extent. It is important, therefore, for the steel mill to have a means of determining from time to time the amount of segregation in the ingot.

To cut sections from the ingot itself for the purpose of making microscopical tests would be very difficult and would interfere seriously with mill operations. An examination of pieces rolled from the top and from the bottom of the ingot answers the purpose.

If an ingot containing segregated material is rolled into any particular shape (angle-iron, beam, rail, plate, etc.) the zone of segregation appears in the rolled piece.

The I-beams shown in Figs. 72 and 73 are rolled from the same basic-Bessemer ingot from which the sections shown in Figs. 70 and 71 were taken. Fig. 72 corresponds to the top of the ingot and Fig. 73 to the bottom. In the beam rolled from the top of

FIG. 74.—From the top of the ingot.

FIG. 75.—From the base of the ingot.

the ingot the dark dividing band between the inner and outer zones is clearly marked while in the other beam no division is evident. The blow holes have disappeared. The agreement between the original ingot and the rolled material with respect to zone formation is clearly shown.

Figs. 74 and 75 are made from basic-Bessemer ingot rolled out to small rods. Fig. 74 represents in this case the top of the ingot, while Fig. 75 is from the lower end. The segregation phenomena are exactly similar to those just described.

Analyses of the inner and outer zones gave the following values:

TABLE 56

	Corresponding to top of ingot		Corresponding to bottom of ingot	
	Center, per cent.	Edge, per cent.	Center, per cent.	Edge, per cent.
Carbon	0.11	0.08	0.09	0.09
Manganese	0.52	0.50	0.48	0.52
Phosphorus	1.125	0.080	0.075	0.080

Here again the differences between the center and edge of the piece rolled from the top of the ingot are considerable while these differences almost disappear in the other piece.

In order to get an idea of the nature of the segregation in a given ingot, the examples given above indicate that it is not enough to take a section from a piece rolled from one end of the ingot but that it is absolutely necessary to have sections corresponding to both ends and under certain circumstances a section representing the center of the ingot

4. Influence of the Method of Sampling on the Analytical Results.—If the samples for analysis are taken without any regard to segregation phenomena, or are taken by an untrained man in an unintelligent way, the most remarkable and widely varying results can be obtained although the analyses may be carried out perfectly.

The following is a general method for getting an average sample from a rolled piece:

If it is at all possible, the samples for analysis should be taken by planing over the entire cross-section and not by boring or drilling. If on the contrary an average sample is not wanted, but it is desired to determine whether or not zone formation due to segregation has taken place, or whether there are other irregularities in the chemical composition of the material, the metallographic examination should precede the sampling.

It will be shown by a number of examples taken from a metallographic practice how greatly the analytical results may be influenced by improper sampling.

It would be altogether wrong, for example, to take samples from a rolled rod by turning off the outer layer as indicated in

Fig. 76. If zone formation has taken place, due to segregation, an analysis of turnings taken at the point *d* on the outer zone *R* would give an entirely false idea of the average composition of the bar as that point represents the part of the bar in which segregation is least strongly marked. If now, in order to make a control analysis, the rod was turned down still more (*e* in Fig. 76) the analyst would find much higher percentages of phosphorus and sulfur, assuming that segregation had taken place as indicated.

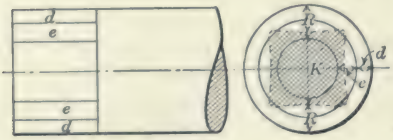


Fig. 76.

A few examples will show how great these differences can be.

(*a*) Shaped Iron.—Fig. 77 is a drawing of a cross-section of a broken bolt. The section after etching with copper ammonium chloride showed a sharply marked separation into a bright outer zone *R* and a dark four cornered inner zone *K*. The dark color of the inner zone indicates phosphorus segregations. The area of the inner zone is greater than that of the outer.

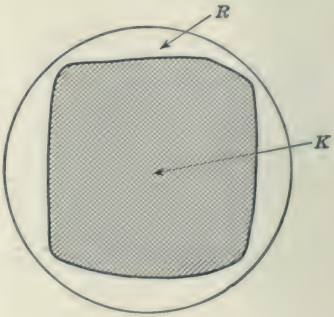


Fig. 77.

Measurement showed:

Inner zone	1552 sq. cm.
Outer zone	823 sq. cm.
Total area	2375 sq. cm.

The phosphorus values were:

Table 57

Sample taken from	Per cent. phosphorus
Outer zone, *R*	0.077
Inner zone, *K*	0.110
Planings from the entire cross-section	0.100

If the average phosphorus content is found by calculation from the percentage in each zone and the area of the zone, the value is 0.099 per cent. phosphorus.[1] This is in very good agreement with the average value given as 0.100 per cent.

Example 2.—Fig. 78 shows the etched surface of a broken connecting rod. The inner core *K* contains numerous dark spots rich in small, non-metallic inclusions. The bright outer zone is

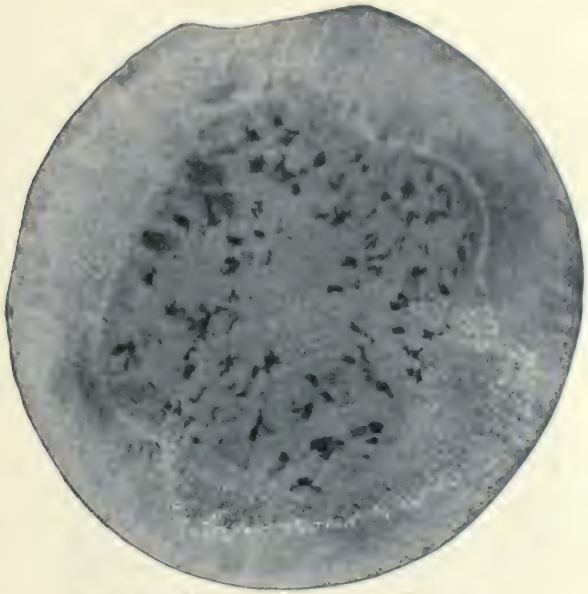


FIG. 78.—Section of a connecting-rod screw.

crossed by dark lines perpendicular to the sides of the quadrangle which bounds the inner zone. These come from the blow holes which were perpendicular to the edges of the original ingot and were closed up during the rolling. The four-cornered cross-section of the inner zone shows that the ingot from which the rod was made was quadrangular in cross-section.

[1] $\frac{1552 \times 0.110}{2375} + \frac{823 \times 0.077}{2375} = 0.099$ per cent. phosphorus.

Analyses gave these values:

TABLE 58

	Inner zone, per cent.	Outer zone, per cent.
Carbon	0.11	0.09
Phosphorus	0.080	0.050
Sulfur	0.080	0.040
Manganese	0.72	0.70
Silicon	Trace	Trace
Copper	0.02	0.02
Nickel	0.07	0.07

Carbon, phosphorus and sulfur have segregated in the inner zone.

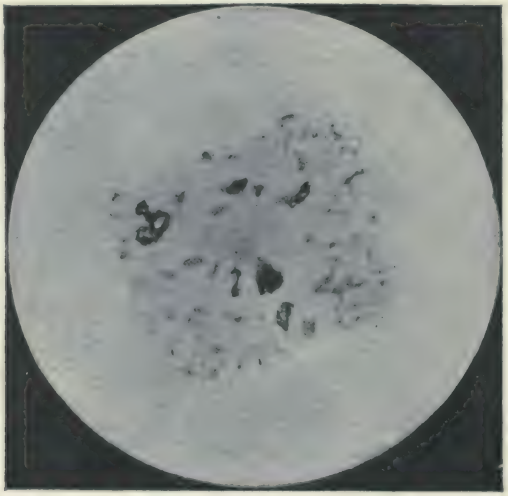


FIG. 79.—Section of a bolt.

Example 3.—Fig. 79 is the cross-section of a bolt. Zone formation due to segregation is clearly marked. Determinations of phosphorus and sulfur gave the following values:

TABLE 59

	Inner zone, per cent.	Outer zone, per cent.
Phosphorus	0.120	0.042
Sulfur	0.080	0.018

The inner zone shows a marked segregation of sulfur and phosphorus.

Example 4.—Fig. 80 is the polished cross-section of a square bar of basic-Bessemer steel. The section shows in the dark colored inner zone numerous small non-metallic inclusions evidently of a sulfidic character. Analyses of the two zones gave:

TABLE 60

	Inner zone, per cent.	Outer zone, per cent.
Carbon	0.092	0.096
Manganese	0.41	0.38
Silicon	0.012	0.014
Phosphorus	0.060	0.050
Sulfur	0.072	0.030
Copper	0.074	0.050
Nitrogen	0.010	0.009

Besides the slight segregation of phosphorus there is a much larger sulfur segregation in the inner zone.

If, in the cases just cited, the samples for analysis had not been taken by planing across the entire section but by boring, it would have been quite possible to obtain unreliable results even if the holes had been drilled all the way through the metal. If, for example, a round rod is drilled as indicated by *I*, Fig. 81, the drillings do not correspond to the average composition as would those made by planing. The relative position of the holes has an influence on the values obtained. (See points *I* and *II* in Fig.

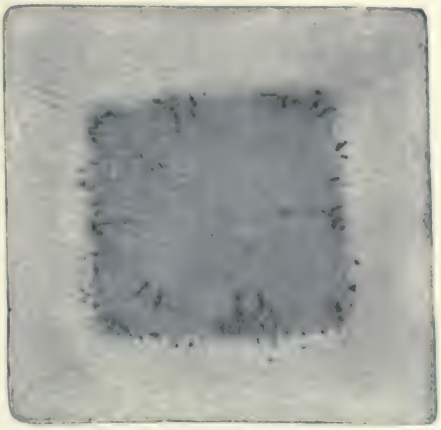


FIG. 80.—Square bar of basic-Bessemer steel.

81.) More drillings from the unsegregated outer zone would be made by a hole at *I* than at *II*. The drillings from hole *I* are therefore poorer in phosphorus and sulfur than those from hole *II*.

These facts hold not only for round or square pieces, but also for those of any other shape if segregation into any inner and outer zone has taken place in the ingot.

Even with correct sampling, analytical differences may occur under certain conditions. Assume, for example, that the material of which the bar or other piece consists was sampled correctly by the shipper by planing over the whole cross-section and a phosphorus determination made. The sample contained "a" per cent. phosphorus. The rod was then turned down by the purchaser and used for construction work. Because of a break, the

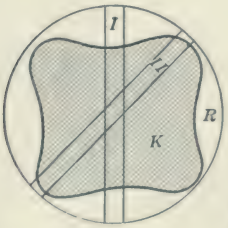


FIG. 81.

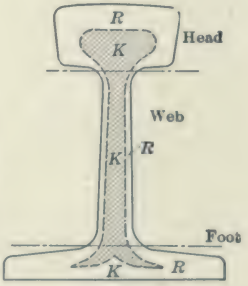


FIG. 82.

finished product was analyzed for phosphorus. In this case too the sample was taken correctly by planing. The average phosphorus content will be greater in this case if the original bar contained a core rich in phosphorus, as the outer zone, low in phosphorus, would have been removed by turning. Microscopic tests would indicate the difference between the original bar and the finished product.

As stated on p. 98 and illustrated in Fig. 72, the segregation zone goes through the various processes of mechanical treatment, rolling, forging, etc., without coming to the surface of the piece. Because of the flowing of the material of the outer zone on rolling, very considerable changes in the relative areas and shapes of the

inner and outer zones may take place. The dark inner zone forms a much larger proportion of the total area in the web of an I-beam (Fig. 72) than in the flanges. The same thing is true in the case of rails and other rolled forms. Fig. 82 is the drawing of an etched rail section. The inner zone is cross-hatched.

FIG. 83.—Cross-section of a mine rail.

The ratio between the areas of the inner and outer zones in the different parts of the rail were as follows:

TABLE 61

	Proportional area of inner zone, *K*, per cent.	Proportional area of outer zone, *R*, per cent.
In head of rail	32.1	67.9
In web of rail	63.4	36.6
In foot of rail	14.4	85.6

Chemical analysis gave the following results:

TABLE 62

	Inner zone K, per cent.	Outer zone R, per cent.
Phosphorus	0.127	0.063
Sulfur	0.060	0.023
Manganese	0.55	0.50

The differences in chemical composition between the inner zone K and the outer zone R are quite marked. A representative sample for analysis can be obtained only by planing over the entire cross-section. Planing part of the section (for example only the upper half) would give incorrect values because of the uneven distribution of the sulfur and phosphorus in the final product. (See Table 61.)

Similar cases of marked segregation are illustrated in the two following examples.

Fig. 83 is the cross-section of a mine rail. Three distinct zones are noticeable.

(*a*) A narrow rim around the outer edge of the section, colored dark by the etching reagent.

(*b*) An intermediate zone R_2 which stays bright after etching.

(*c*) An inner zone made very dark by etching and containing many small, non-metallic inclusions, probably due to deoxidation.

Chemical analysis gave:

TABLE 63

	Inner zone, K, per cent.	Outer zones, R_1 and R_2, per cent.
Phosphorus	0.158	0.115
Sulfur	0.064	0.042

Owing to the peculiar distribution of the zones which are rich in phosphorus, the average phosphorus content in the two outer zones $R_1 + R_2$ is also high.

Fig. 84 shows the section of an iron girder with marked zone formation due to segregation. Analysis gave:

TABLE 64

	Inner zone, per cent.	Outer zone, per cent.
Phosphorus	0.11	0.06
Sulfur	0.13	0.06

Phosphorus and sulfur, which give the dark inner zone in Fig. 84, are high.

(*b*) IRON PLATE AND HOOP IRON.—Errors are frequently made in taking samples from plates. Several examples will be given to show how great the differences can be in different parts of the surface and how necessary it is in many cases that the chemical analysis should be preceded by a microscopical examination.

(*a*) The following case is a classic example of the difficulty.[1]

A very red-short boiler plate was analyzed for sulfur by a number of chemists. Samples of the steel were sent in sealed packages to the various laboratories and the results returned varied from 0.067 per cent. to 0.240 per cent. sulfur. The differences were altogether greater than possible differences due to different methods or to experimental errors.

A metallographic study explained the situation at once. Marked zone formation had taken place due to segregation as shown in Fig. 85. After locating the segregated areas, borings were taken from the different zones and gave on analysis the following sulfur values.

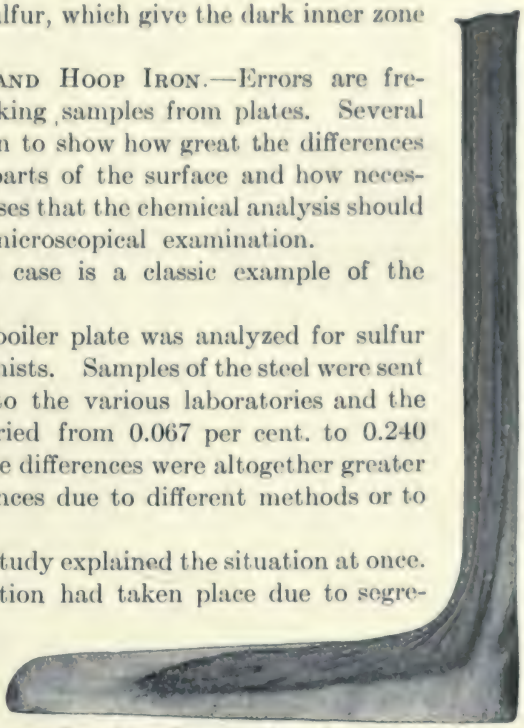


FIG. 84.—Cross-section of an iron girder.

TABLE 65.—ANALYSES BY HEYN

Sample taken from	Sulfur, per cent.
Zone *I*	0.067
Zone *II*	0.201
Zone *III*	0.240

[1] See Heyn and Bauer, "Metallographie," Part 2, p. 132.

The samples submitted to the different laboratories were evidently incorrectly taken by drilling or planing in different places so that one laboratory had samples from the low sulfur zone *I*, another from area *II* which was somewhat richer in sulfur and a third from the most segregated area *III*. A true average sample could be taken only by planing over the whole cross-section.

Example 2.—Fig. 86 is a drawing of the section of very brittle boiler plate. Even before etching, the section showed two clearly marked streaks γ and ϑ.

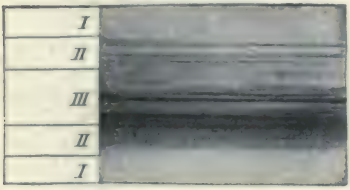


FIG. 85.—Red short boiler plate.

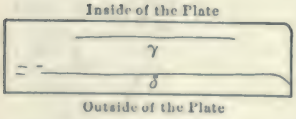


FIG. 86.—Outside of the plate.

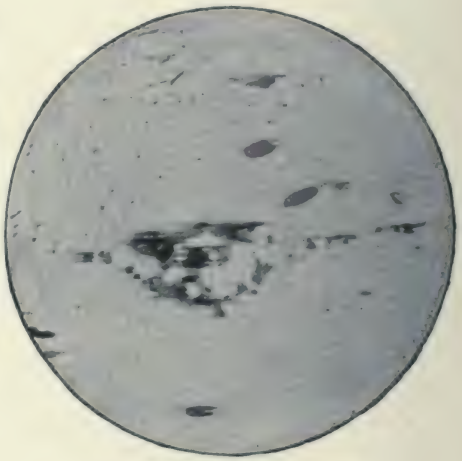


FIG. 87.—Sulfide inclusions.

Microscopically small, bluish, non-metallic inclusions such as frequently occur in wrought iron are particularly noticeable in the zone between the lines γ and ϑ, and small, yellowish-gray inclusions are found in the lines.

Fig. 87 shows a group of such inclusions magnified to 123 diameters. The appearance of the inclusions indicates that segregation of metallic sulfides has taken place along the lines γ and δ as well as in the zone lying between them. The print on silk (*cf.* p. 15) shown in Fig. 88 confirms this suspicion.

Sulfur determinations made on samples taken as indicated in sketches *a*, *b*, and *c*, Fig. 89, gave the following values:

TABLE 66

Test specimens taken	Sulfur, per cent.	Phosphorus, per cent.
From the outer layer as shown in Fig. 89*a*	0.04	0.088
Near the streaks as shown in Fig. 89*b*	0.16	0.203
By planing over the whole cross-section, as in 89*c*.	0.10	0.168

After etching with copper ammonium chloride the section shows a very dark-colored core and two somewhat lighter outer layers. (*cf.* Fig. 90.)

The bend in the streak at the rivet hole indicates that the rivet was punched and not drilled. The streaks γ and δ are brought out more clearly by the etching. They are composed of large prismatic ferrite crystals which are considerably larger than the surrounding crystals of ferrite. Fig. 21 (p. 27) shows the line γ magnified about 4 diameters.

FIG. 88.—Sulfur print on silk.

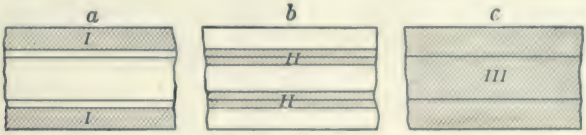


FIG. 89.

The very dark color after etching with copper ammonium chloride and the large size of the ferrite crystals indicate an especially

FIG. 90.—Section etched with copper ammonium chloride.

high phosphorus content in the streaks. Analyses gave the values shown in Table 66. Sulfur and phosphorus are both very high in the neighborhood of the dark lines.

Example 3.—Similar conditions were found in the section of a ship-plate. Fig. 91 shows the cross-section after etching with copper ammonium chloride.

The photograph shows: A light outer zone, a darker inner zone filled with small dark streaks, and two particularly dark stripes between the inner and outer zones. Analysis shows:

FIG. 91.—Cross-section of a ship-plate.

TABLE 67

Samples taken	Phosphorus, per cent.
From the outer zone	0.088
From the inner zone	0.119
From and near the dark streaks	0.200

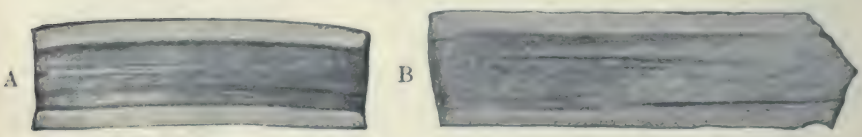


FIG. 92.—Sections of ship-plates.

FIG. 93.—Section of a ship-plate.

Because of the thinness of the lines in this case as in the other it was necessary in sampling to take part of the material from the immediate neighborhood of the lines, so that the phosphorus content of the material in the dark streaks is really greater than the analysis shows.

Figs. 92 and 93 show etched sections of three ship-plates, *A*, *B*, and *C*. All three showed marked zone-formation due to segregation. Analyses gave:

FIG. 94.—Sulfur prints on silk.

TABLE 68

Samples taken from	Phosphorus, per cent.	Sulfur, per cent.
Plate *A* Outer zone	0.08	Not determined
Inner zone	0.16	Not determined
Plate *B* Outer zone	0.153	0.069
Inner zone	0.282	0.180
Plate *C* Outer zone	0.140	0.066
Inner zone	0.250	0.150

Example 4.—It frequently happens that the segregation areas are not so sharply marked as in the cases just described, but that smaller or larger segregated spots are irregularly distributed throughout the whole cross-section area. In this case there is no distinct division into an inner and outer zone.

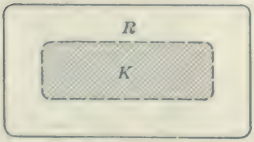


FIG. 95.

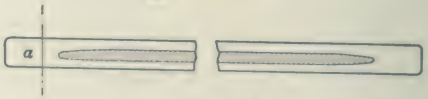


FIG. 96.

Fig. 94 shows the sulfur prints on silk of three plates in which the segregation stripes are irregularly distributed. Analysis gave:

TABLE 69

Sample taken	Phosphorus, per cent.	Sulfur, per cent.
Over the whole cross-section	0.078	0.06
From the segregated streaks	0.183	0.101

In all these cases, representative samples could be taken by planing over the whole cross-section. In some cases, however, even shavings made by planing over the whole cross-section do not represent the average composition of the material.

If a slab with an inner zone, *K*, like that indicated in Fig. 95, is rolled out to a plate, the inner zone tapers toward the ends and

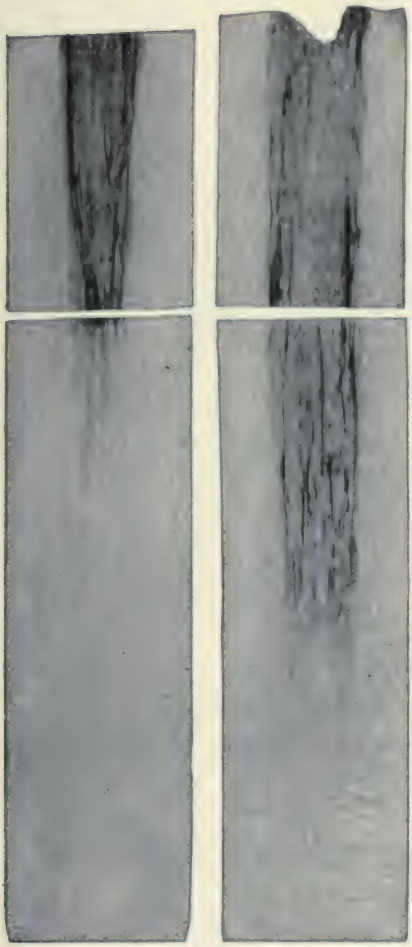


FIG. 97.—Wedge formation of the inner zone in boiler plate.

sides of the plate as indicated in the sketch, Fig. 96, and in the photograph, Fig. 97.

If now, for the purpose of getting samples, the entire section is planed over at the place "*a*" in Fig. 96 the analysis will not show the true average composition of the material in spite of the apparently correct sampling, because the shavings really represent only the outer zone *R*.

Analysis of a plate with a tapering inner zone like that shown in Fig. 97 gave the values:

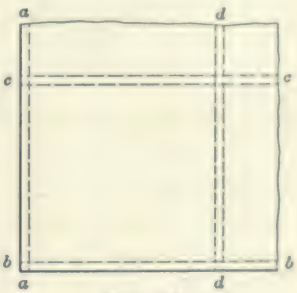


FIG. 98.

TABLE 70

Samples taken	Phosphorus, per cent.	Sulfur, per cent.
By planing over the whole cross-section at "*a*" (Fig. 96), *i.e.*, only from the outer zone	0.048	0.033
Planing over the section to include both outer and inner zones	0.085	Not determined
From the inner zone, *K*	0.110	0.101

To avoid mistakes of this sort in sampling iron or steel plates, not only for chemical but also for metallographic work, the planings or section should be taken not at the edges of the plate *a–a* or *b–b* in Fig. 98 but at *c–c* or *d–d*.

A quite similar tapering of the inner zone toward the two sides

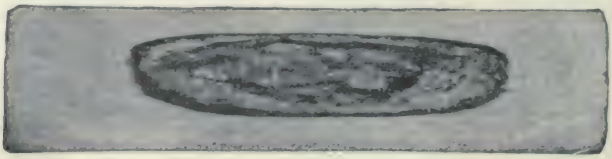


FIG. 99.—Cross-section of hoop iron.

is shown in Fig. 99, the cross-section of an iron hoop. The total cross-section area was 1450 sq. mm. of which the

Outer zone = 780 sq. mm. or 67.6 per cent. of the total area.
Inner zone = 470 sq. mm. or 32.4 per cent. of the total area.

Chemical analysis gave:

TABLE 71

Samples taken	Phosphorus, per cent.	Sulfur, per cent.
From outer zone, *R*	0.083	0.023
From inner zone, *K*	0.140	0.028
After planing the cross-section	0.100	0.027

If the average composition of the sample is calculated from the phosphorus content of each zone and its proportional area, the value found is 0.10 per cent.[1]

This agrees very closely with the value found by direct analysis. In this case, too, the effect of planing the hoop lengthwise and at the surface would have been to cut only the outer zone and incorrect analytical values would have resulted.

[1] $\frac{470 \times 0.140}{1450} + \frac{980 \times 0.083}{1450} = 0.10$ per cent. phosphorus

CHAPTER X

WROUGHT IRON

The same rules hold for getting average samples from wrought iron as in the cases of cast and ingot iron. Whenever possible the shavings should be made by planing over the whole cross-section.

As wrought iron generally contains considerable slag, which on planing would be reduced to a fine powder, all the precautions for the proper collection of borings described in detail on p. 35 should be observed, as otherwise serious losses can occur.

The powdery part is high in oxidic compounds and also rich in phosphorus and silicon. It is necessary therefore in this case to weigh out the powder and the shavings separately in the ratio of their amounts in the sample. (*cf.* p. 60.) The following illustration will explain this.

In sampling a wrought-iron bar, 40 g. of shavings were obtained including 0.905 g. of powdery material.

Analysis gave the values:

TABLE 72

	In the coarse shavings, per cent.	In the powder, per cent.
Carbon	0.10	
Silicon	0.09	Not determined
Manganese	0.21	Not determined
Phosphorus	0.32	0.44
Sulfur	0.03	Not determined
Copper	0.09	Not determined

In sampling a wrought-iron boiler plate, 42 g. of shavings and 1.3 g. of powder were obtained. Silicon and phosphorus determinations gave the values:

TABLE 73

	In the coarse part	In the powder
Silicon	0.06	0.30
Phosphorus	0.23	0.37

The powder is high in phosphorus and in silicon.

The lack of homogeneity in wrought iron is due to the method of manufacture. Much of the material sold as wrought iron is

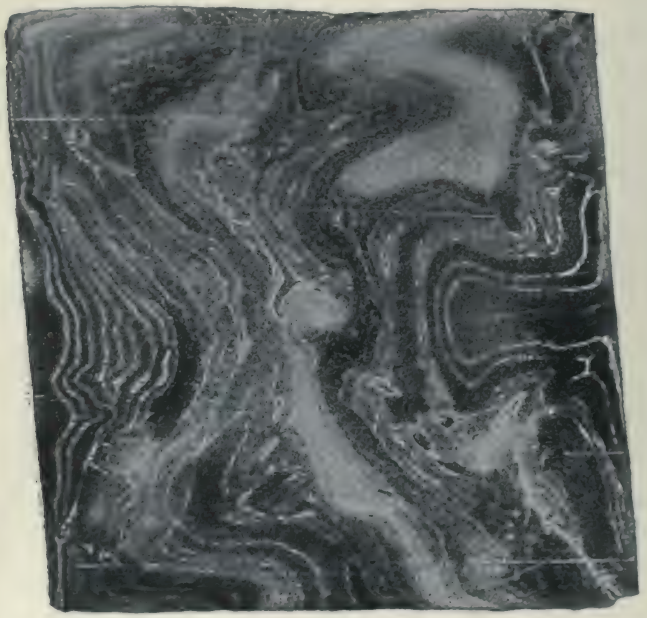


FIG. 100.—Wrought iron made by busheling scrap iron.

made by busheling scrap into a pile and rolling it down. With such material the analytical results obtained depend largely on the places from which the samples are taken.

Fig. 100 is characteristic of iron which has been produced in this way. By etching with copper ammonium chloride, it can be seen without the microscope that the iron is made up of different materials. Samples taken from different parts of a similar

iron gave on analysis carbon percentages varying from 0.11 per cent. to 0.40 per cent.

In the case of puddled iron, the differences are due chiefly to the irregular distribution of the slag and the presence therefore of phosphorus-, silicon- and oxygen-rich spots in the product.

Fig. 101 is the cross-section of a link of puddled iron. The very

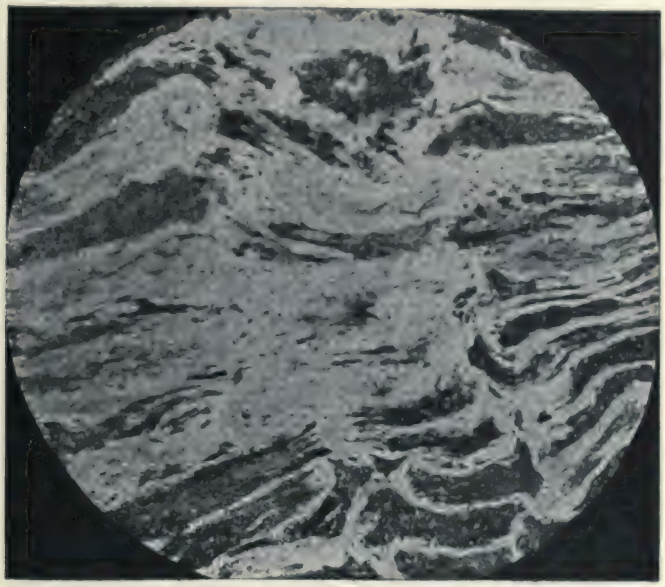


FIG. 101.—Puddled iron.

dark spots in different parts of the area indicate local areas rich in phosphorus. Analysis gave:

TABLE 74

Samples taken	Phosphorus, per cent.
By planing over the cross-section	0.17
By boring in the dark spots	0.30

In a boiler plate, planing over the section showed 0.18 per cent. phosphorus, while borings from the dark spots gave 0.29 per cent.

Figs. 102 and 103 show etched specimens of wrought iron. The

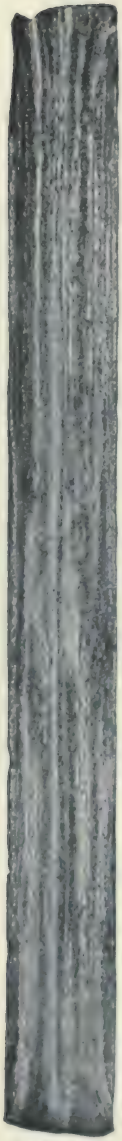


FIG. 102.

FIG. 103.

fairly uniform distribution of the dark areas over the entire surface in Fig. 102 indicates a high average phosphorus content. Analysis gave 0.25 per cent.

Fig. 103 shows that in this case the areas rich in phosphorus are local. The values found were:

TABLE 75

Sample taken	Phosphorus, per cent.
By planing over the whole cross-section	0.07
By boring in the dark streaks	0.16

These illustrations show that in the same specimen of wrought iron great differences of composition may occur in different parts of the cross-section and of the longitudinal section. In contrast to ingot iron, where the segregation is confined as a rule to definite, and sharply marked zones, in wrought iron they are irregularly distributed over the whole surface of the section.

To obtain even an approximately representative sample of wrought iron it is necessary, therefore, to take samples by planing over the entire surface of various parts of the piece and to unite the various shavings. The necessity of collecting the fine powder has been emphasized already.

In wrought iron, the third significant figure is valueless in the percentage found by analysis (even for phosphorus and sulfur) because of the variations in the composition of the original material.

CHAPTER XI

SAMPLING IN SPECIAL CASES

In some cases local changes in the composition are intentionally produced during manufacture. Cementation causes such a change. The purpose of this process is to give a hard surface to a piece of soft material by increasing its carbon content at the surface.

In a case of this kind an average analysis for which the samples are obtained by planing over the entire cross-section is of little value. The important question is to determine how much carbon has been taken up and the depth of the carbon-rich zone. In all cases metallographic examination should be made before the sample is taken.

Frequently the piece is quenched from red heat after the cementation process (case hardening). The outer layer, richer in carbon, becomes hard, while the inner core remains soft. If such a hardened piece is to be analyzed it must be annealed so that it may be worked. Special care must be taken during the annealing not to lose carbon by surface oxidation. The precautions to be taken have been described on page 36. Moreover, care must be taken to avoid a transfer of the carbon from the richer outer layer into the interior. The annealing time, therefore, is made as short as possible (about ¼ hr.) and the annealing temperature is to be kept as low as possible (750° to 800° C.). If the specimen in question is ordinary carbon steel (not a special steel) it may be quenched in water after the furnace temperature has fallen below 700°, as hardening does not take place below the pearlite point. If these precautions are taken during the annealing the transfer of carbon is very slight.

If the annealing furnace is kept at a high temperature (1000° or higher) and the time is unduly prolonged (several hours for example) a marked diffusion of the carbon into the low-carbon area takes place. The chemical and microscopical study then gives a wrong idea of the original distribution of the carbon in the

sample. The following illustration shows how great this change can be.

Arnold and M. Williams[1] fitted a piece of steel with 1.78 per cent. carbon into a cylinder of iron nearly free from carbon and heated 10 hr. in a vacuum at 1000°. Fig. 104 shows the distribution of the carbon after the heating. The dark inner part is the steel core and the outer part the iron shell. The circles represent the different layers which were removed successively and analyzed for carbon. The inscribed percentages show clearly the gradual diffusion of the carbon from the steel to the soft iron.

Metallographic examination shows with great sharpness the depth of the carbonized layer and gives at least an approximate idea of the increase in carbon content.

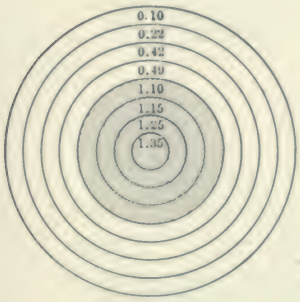


FIG. 104.

FIG. 105.—Section of a case-hardened axle-bearing.

Fig. 105 shows with fourfold magnification the cross-section of a small case-hardened axle-bearing. The thickness of the carbon-rich layer *R* (light in the photograph) was about 0.55 mm. The outer zone *R* contained 0.95 per cent. carbon while the core *K* (dark in the photograph) had only about 0.1 per cent. There was a fairly sharp transition from the high-carbon content of zone *R* to the low-carbon zone *K* as shown in Fig. 106 with a magnification of 117 diameters.

[1] J. Iron and Steel Institute, **1899**, 85.

A similar change from an outer zone, R, rich in carbon, to an inner zone, K, containing less carbon, is shown in Fig. 107 (magni-

M = 117

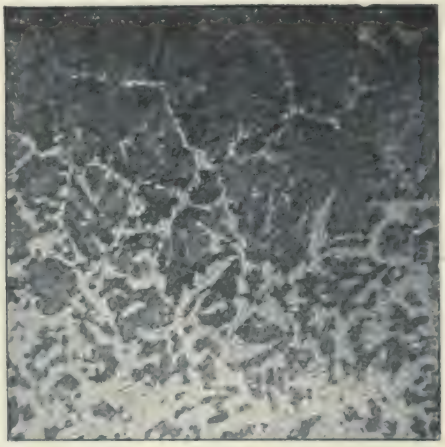


FIG 106.—Transition from K to R.

M = 29

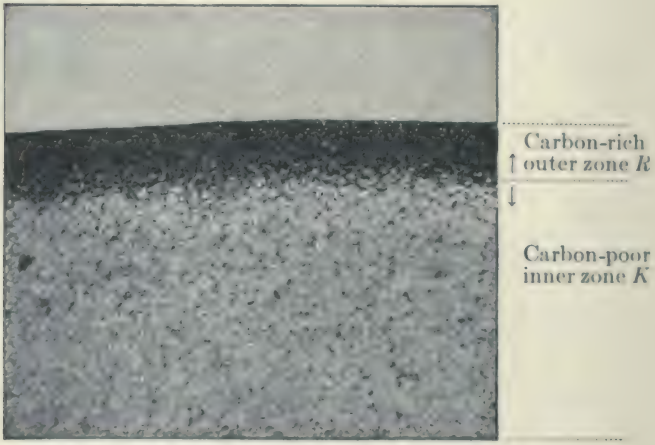


FIG. 107.—Transition from K to R.

fied 29 diameters). The photograph shows a section of a hardened axle. The axle was annealed before the investigation, as

the outer zone was glass hard and could not be machined. The thickness of the high-carbon zone was only about 0.3 mm. Fig. 107 also shows that with a low annealing temperature and a short time of exposure, the danger of a diffusion of carbon is very slight.

Two case-hardened steel balls *A* and *B* showed a carbon-rich outer zone of about 1 mm. thickness. Analysis gave the following:

TABLE 76

	Ball *A*		Ball *B*	
	Outer zone, per cent.	Inner zone, per cent.	Outer zone, per cent.	Inner zone, per cent.
Carbon.....	0.59	0.31	1.25	0.99

In all cases of this type the outer, high-carbon zone is first turned off after its thickness has been determined by the microscope. Samples of the inner zone are then taken by planing over its cross-section.

Long heating in an atmosphere rich in oxygen causes a change exactly the reverse of that just described; a decarbonization of the outer layer takes place. Fig. 108 shows a piece of cast steel in natural size.[1] Etching with copper ammonium chloride causes a darkening of the core which is rich in carbon and thus gives a good idea of the depth of the decarbonization. The transition from the decarbonized outer layer to the carbon-rich inner zone is shown in Fig. 109 with a magnification of 117 diameters. Microscopic examination gives a clear idea of the amount of decarbonization without the necessity of analysis. Similar phenomena play a very undesirable part in the behavior of tool steel. The decarbonization is often confined to a very thin layer or occurs locally. If this partial decarbonization takes

FIG. 108.—Steel casting superficially decarbonized by too long annealing.

[1] E. Heyn, Stahl u. Eisen, **1906**, No. 10.

place exactly where hardness is required, difficulties arise which can be overcome only if the cause is known. A chemical analysis without a previous metallographic examination would be valueless in cases of this sort, where accidental and unexpected local changes in the chemical composition of the steel have occurred.

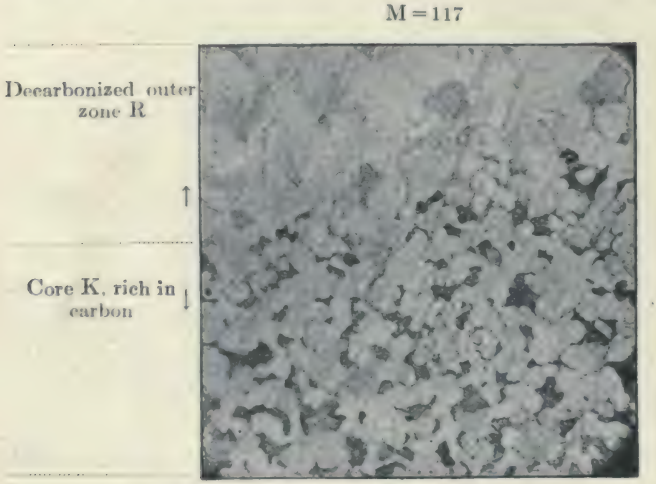


FIG. 109.—Transition from R to K.

CONCLUSION TO PART I

The typical examples described in Chapters VII to XI will show to what a marked extent analytical results are dependent on the method of sampling. It is possible that the analytical results may vary between quite wide limits, depending on how and where the sample was taken (Chapter VII).

Naturally these conditions give rise to the opportunity for unjust criticism. This can be successfully met by the analyst only when he is trained in metallography and when the responsibility for the sampling as well as for the analysis is in his hands.

PART II

ANALYSIS OF IRON AND STEEL

BASED ON THE GERMAN TEXT

OF

EUGEN DEISS

TRANSLATED WITH MANY ADDITIONS, CONFORMING TO LABORATORY PRACTICE IN THE UNITED STATES

BY

WILLIAM T. HALL

CHAPTER I

CARBON

Carbon occurs in iron and steel in the combined form as carbide, as a solid solution of iron carbide in iron, and in the uncombined state as graphite or as temper carbon.

Absolutely reliable methods for the determination of combined carbon in the presence of free carbon are not known but it is possible to determine the total carbon and that which is uncombined. In order, therefore, to determine the amount of combined carbon in a sample, the total carbon and free carbon are determined separately and the combined carbon found by difference.

Graphite and temper carbon cannot be separated by chemical means. It is possible in many cases, by means of the metallographic methods described in the first part of this book, to find out whether the free carbon is present as graphite or as temper carbon.

DETERMINATION OF TOTAL CARBON

The methods for the determination of carbon by direct combustion of the sample give results which are doubtless more accurate than the older methods based on the removal of the iron (by the use of copper salt solutions, mercuric salt solutions, chlorine gas, etc.) with a subsequent combustion of the residual carbon.[1] Since direct combustion methods are also more rapid than other methods they are to be preferred to all others.

Direct combustions can, in general, be made in one of two ways:

1. The wet method (Corleis' chrome-sulfuric acid process) or
2. The dry method (combustion with oxygen in an electrically heated tube furnace).

[1] *cf.* Dillner in the report on the various Methods for the Determination of Carbon and Phosphorus in Iron and Steel by Jüptner v. Jonstorff, Blair, Dillner and Stead, J. Iron and Steel Inst., **1904**, and Bull. Am. Inst. Min. Eng., **1905**, 289 and 643.

1. COMBUSTION IN THE WET WAY. CORLEIS' CHROME-SULFURIC ACID METHOD[1]

Principle.—Iron and steel samples of suitable fineness are dissolved by boiling with a mixture of chromic and sulfuric acids, which causes the simultaneous oxidation of nearly all the carbon to carbon dioxide. A little of the carbon is usually set free as carbon monoxide or as hydrocarbon unless certain precautions are taken. Corleis found that the formation of such carbon compounds is greatly reduced by the addition of copper sulfate solution, but it is always best to heat the gases mixed with air in order to be certain that all the carbon is in the form of carbon dioxide. The carbon dioxide formed is absorbed by soda-lime contained in a U-tube or by caustic potash solution in a Geissler bulb. From the gain in weight, the amount of carbon in the sample is calculated.

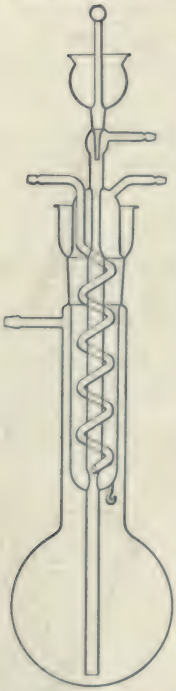


FIG. 110.

Apparatus and Necessary Solutions.—For combustion with chrome-sulfuric acid, the Corleis flask K with condenser is used (Fig. 110).[2] There is a ground-glass connection between the condenser and the flask.

To keep the flask from breaking when it is heated, either support it on wire gauze or cover the bottom with asbestos paper as shown in Fig. 111. In the latter case, cut out suitably shaped pieces of asbestos paper (about 0.5 mm. thick), wet them with water, stick them to the bottom of the flask, and allow them to dry a little while in a drying closet at 110°.

The arrangement of the entire apparatus is shown in Fig. 111. Air is passed through the apparatus either by applying suction at W or from a gasometer leading to W_1. To purify the air, place concentrated caustic potash solution (1:1) in the wash bottles W_1 and W_2 and soda lime in the U-tube, U. Instead of these

[1] Stahl u. Eisen, **14**, 381 (1894).

[2] The apparatus may be obtained from Bleckmann and Burger, Auguststr. 3, Berlin, Germany.

three tubes, a single soda-lime tower, with concentrated caustic potash solution at the bottom may be used.[1]

The gases from the combustion flask pass first through a small wash bottle, *S*, containing concentrated sulfuric acid. The glass tubing through which the gas enters should not dip into the sulfuric acid, but should end a few millimeters above the surface of the liquid. This flask has the function of holding back water vapor and sulfuric acid fumes, from the boiling solution, without any danger of retaining appreciable quantities of the hydrocarbons in the sulfuric acid.

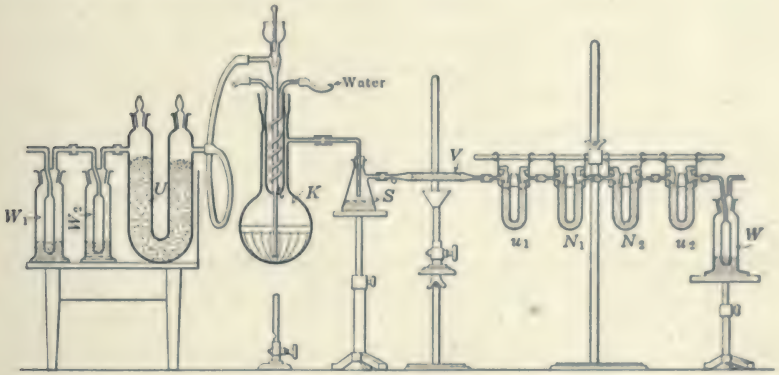


FIG. 111.

To *S*, attach a small combustion tube, *V*, made of difficultly fusible glass or of porcelain and containing copper oxide or platinized asbestos.[2]

If a glass tube is used, wrap it in iron gauze to prevent it from breaking when heated. The purpose of this combustion tube is to convert traces of carbon monoxide, or of hydrocarbons, into carbon dioxide.

The use of copper sulfate in the oxidizing liquid, however, prevents the loss of more than 2 per cent. of the total amount of carbon present in any sample of ordinary iron or steel. In

[1] *cf.* Treadwell-Hall, Text-book of Analytical Chemistry, Vol. II, p. 400 (1914).

[2] The platinum capillary combustion tubes so frequently recommended have not given satisfaction; on continued use the platinum crystallizes and becomes permeable to gases.

commercial work, therefore, this combustion tube may be omitted. Moreover, an inspection of the results obtained in test analyses with pure sodium oxalate (*cf.* p. 136) shows that the tendency of the method is to give results that are slightly high, which is another reason why this combustion tube may be omitted. In that case, connect the flask K directly with a small tube containing solid chromic-acid anhydride, between plugs of glass wool, and from this lead the gas into a U-tube containing a few glass beads wet with concentrated sulfuric acid. Place a little glass wool in each arm of this U-tube to break up any bubbles of sulfuric acid that may form during the analysis. Then, with the omission of S and of V, the arrangement is the same as shown in the drawing.

The last traces of moisture must be removed from the gases before the carbon dioxide is absorbed. This is accomplished by means of the small U-tube, u_1, containing calcium chloride or phosphorus pentoxide between plugs of cotton wool.

From this drying tube, the gases pass into the weighed soda-lime tubes N_1 and N_2, in which the carbon dioxide is absorbed. Usually all of the carbon dioxide is absorbed in the first tube. If the second tube begins to gain in weight, it is a sign that the first tube is nearly exhausted. When this happens, refill the first tube and then use it as the second tube in the train.

When carbon dioxide reacts with soda-lime, water is set free. To prevent the loss of this moisture, each tube must contain a little calcium chloride or phosphorus pentoxide. Fill the arm through which the gas enters with small pieces of soda-lime and fill half of the other arm with soda-lime. Then cover the soda-lime with a small piece of glass wool and fill up the tube with dry calcium chloride (or phosphorus pentoxide). In the top of each arm of the U-tube, place a plug of cotton wool. The kernels of soda-lime and of drying agent should be from 1 to 1.5 mm. in diameter; if much powder is present, it must be sifted out to avoid stopping up the tube. Too large lumps of either soda-lime or drying agent must not be used and the tubes must be filled tightly, or some gas may escape that should be absorbed.

As an added precaution, the second soda-lime tube is connected with a calcium chloride (or phosphorus pentoxide tube) u_2 and this in turn is connected with a safety wash bottle, W, containing concentrated caustic potash solution; there is then no chance of

water vapor or carbon dioxide being drawn back into the weighed tubes from the atmosphere. The wash bottle, *W*, also serves to indicate the rate at which the gas is passing through the apparatus.

Connections between the different parts of the apparatus are made by rubber tubing. In setting up the apparatus, take care that all the connections to the right of the Corleis flask are tight (glass on glass); in no case should the ends of the glass tubing be separated by empty sections of rubber tubing.

The following solutions are necessary:

(*a*) *Chromic Acid Solution.*—Dissolve 720 g. of chromic acid anhydride, which need not be chemically pure but should be practically free from organic matter, in 700 cc. of water.

(*b*) *Copper Sulfate Solution.*—Dissolve 400 g. of copper sulfate crystals in water and dilute the solution to 2 liters.

Preliminary Boiling of the Chrome-sulfuric Acid Solution.—Remove the condenser from the flask *K*, and introduce 35 cc. of the chromic-acid solution (*a*), 150 cc. of the copper sulfate solution (*b*) and 200 cc. of concentrated sulfuric acid (sp. gr. 1.84).

Replace the condenser and start a stream of water running through it. Boil the mixture in the flask to remove any organic matter which may be present, with the soda-lime tubes disconnected from the flask. While the solution is boiling, pass a slow stream of purified air through the apparatus and heat the small combustion tube *V*. Boil the solution for at least an hour in order to be sure that in subsequent work no carbon dioxide, or other gases absorbed by soda-lime, will be generated from carbon in the reagents. Then remove the flame and allow the apparatus to cool in a current of air.

Before starting an analysis it is advisable to run a blank on the apparatus, to find out how much the soda-lime tubes change in weight without the introduction of any substance to be analyzed.

Blank Run.—Rub the soda-lime tubes with a piece of chamois or a clean linen cloth, allow them to stand in the balance case for at least half an hour, then open the stopcocks for an instant to equalize the pressure and weigh them accurately to 0.0002 g. Connect the weighed tubes to the rest of the train, open the stopcocks and pass a slow stream of air free from carbon dioxide through the apparatus. Boil the contents of the Corleis flask and heat the combustion tube for 2 or 3 hours (the usual length

of time for a combustion). Then remove the soda-lime tubes, close the stopcocks and place the tubes in the balance case. Remove the flame from beneath the Corleis flask and weigh the tubes, under the same conditions as before, after they have remained at least half an hour in the balance case.

If much more than 0.001 g. gain in weight is found in the blank determination, something is wrong. Besides possible impurities in the chromic acid, it may be that small particles of soda-lime or of drying agent have lodged in the glass tubing beyond the stopcocks, either due to a too rapid passage of the air current or to faulty filling of the tubes. In such a case the tubes would gain in weight constantly if left in the air, owing to absorption of carbon dioxide or of water. Care should be taken, therefore, to see that the tubing is free from soda-lime or drying agent. If necessary, the inside of the tubes may be wiped clean with small rolls of filter paper.

Slight gains in weight in the absorption tubes, which are almost always observed in the blank, should be allowed for in the determination. For further information on this point see p. 135 and Table 77.

Procedure.—While the acid solution in the flask is cooling, weigh the soda-lime tubes as previously described and also the sample of iron or steel, the carbon content of which is to be determined.

The weight of sample taken for analysis should be determined by its probable carbon content. Of cast iron, with 3 per cent. or more of carbon, take 1 g.; of steel with 0.3 per cent. or more take 3 g.; and of mild steel or wrought iron take 5 g.[1] Weigh the

[1] In weighing out samples it is a waste of time to weigh accurately to decimal places beyond those which affect the analysis. In the determination of carbon in steel, the absolute accuracy is determined largely by the degree of accuracy to which the soda-lime tubes, used for absorbing the carbon dioxide, can be weighed. Unless particular precautions are taken, such as reducing the weighings to vacuum, etc., the difference between the weights of the soda-lime tubes before and after the analysis cannot be assumed to be nearer than 0.001 g. to the truth. As a general rule, the next to the last significant figure in any value should not vary by more than one or two units. According to this rule, therefore, the soda-lime tubes should be weighed as carefully as possible to four decimal places, which is possible with the usual analytical balance. In the case of a sample of steel with 1

sample into a porcelain crucible, a glass-stoppered weighing tube, or, if it can be obtained in powder form (*e.g.*, gray cast iron), into a small glass bucket which can be suspended, by means of fine platinum wire, from the hook which is usually provided on the end of the condenser, so that the sample is immersed in the liquid in the flask.[1] After the chrome-sulfuric acid solution has cooled sufficiently, connect the soda-lime tubes with the apparatus and pour a little sulfuric acid into the funnel at the top of the condenser to act as a seal; then test the entire apparatus to see if it is tight. To do this, close all the stopcocks in the absorption train and open the cock at the air supply to the Corleis flask. After a short time no more bubbles should pass through the Corleis flask. If bubbles do form, a leak is indicated between the Corleis flask and the phosphorus pentoxide tube u_1. When this section is found to be tight, open the first stopcock in the calcium chloride (or phosphorus pentoxide) tube; if after waiting a short time the current of air through the Corleis flask again stops, open the next stopcock and so on up to the last stopcock on the final calcium chloride tube u_2. After the apparatus has been shown

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per cent. carbon, a 3 g. sample will yield 0.110 g. of carbon dioxide and an error of 0.001 g. in this weight will correspond to 0.01 per cent. carbon, or to one-hundredth of the entire carbon content. This precision is satisfactory here. An error of 0.03 g. in the original weight would correspond to the same fractional error. If, therefore, the original sample is weighed to the nearest centigram, any error introduced by neglecting the following decimal places will not have an appreciable effect upon the final result and any balance accurate to 0.01 g. can be used for weighing out the sample. It is not only a waste of time, but unscientific in principle, to determine values smaller than those which have a noticeable effect upon the result.

In weighing out smaller samples it is usually necessary to weigh more accurately but with cast iron the sample is rarely perfectly homogeneous so that in carbon determinations even with a 1 g. sample, it is sufficient if the original weighing is accurate to 0.01 g.

[1] For obtaining representative samples and for the method of weighing small samples for analysis the precautions mentioned in the first part of the book (*cf.* p. 59) should be taken.

The shavings for the combustion with chrome-sulfuric acid treatment should not be more than 1 mm. thick if the combustion is to be finished in 2 or 3 hr. Thicker pieces should be hammered, broken or rolled before cutting. Hard drawn wire or high-silicon tungsten steel often requires 3 or 4 hr. for combustion even if it is finely divided.

to be tight[1] and the air supply has been shut off, slowly open the last stopcock so that the excess of air will escape from the apparatus without rushing. A sudden rush of air might carry calcium chloride (or phosphorus pentoxide) dust either into or out of the weighed tubes, in each case causing a change in weight.

When the excess of air has escaped, remove the condenser and pour the weighed sample into the flask, or, if the sample has been weighed into a small glass basket, hang this on the hook. Replace the condenser at once and pour a little strong sulfuric acid over the connection between the condenser and the flask to make a tight joint. Raise the condenser again, just a trifle, so that a little of the sulfuric acid can run into the flask to wash down any particles of the sample which may have stuck to the glass.

Now light the gas under the combustion tube *V* and cause a slow stream of air, free from carbon dioxide, to pass slowly through the apparatus. Heat the Corleis flask, slowly at first, until the acid boils.[2]

Continue the boiling for about 3 hr., which is usually long enough to insure the complete solution and oxidation of the sample, unless it was in too coarse a condition. During this time the apparatus should be watched to see that the acid does not boil too violently, and that the air is run at the proper rate, not more than three bubbles a second. At the start if the contents of the flask are heated too quickly, particularly just before the solution boils, there is some danger of liquid sucking back toward the purification train. This is prevented by lowering the flame and increasing the speed of the air current. If, by accident, some of the liquid gets back into the tube *U*, the determination is spoiled. During the last 15 min. of the boiling, it is well to increase

[1] If, instead of using an air reservoir in the experiment, suction is applied at the other end of the train, the manner of testing for leaks is the reverse. Gentle suction should be used in making the test and care should be taken not to let the air in too rapidly after the test.

[2] The current of air must be started as soon as the sample has been introduced. As the cold chromic-acid mixture has slight oxidizing power it is possible for small amounts of hydrogen and hydrocarbons to form. If these gases are not diluted and removed by the air current, they form mixtures with the air in the apparatus which, at certain concentrations of hydrogen and hydrocarbon, may explode in the combustion tube.

the rate at which the air is passing so that it will drive over the last traces of carbon dioxide into the absorption train.

When the combustion is complete, stop the current of air and turn out the gas flames. Close the stop-cocks of all the U-tubes that are in front of the flask and remove the soda-lime tubes. Allow these tubes to stand in the balance case for at least half an hour and weigh them with the usual precautions.

When the contents of the Corleis flask have cooled, remove the condenser and observe carefully whether there is any undissolved sample in the bottom of the flask. In case of doubt, this can be easily seen by pouring the contents of the flask into a large beaker containing considerable water. In most cases this is unnecessary and the solution may be used again for another determination. The quantities of reagents used are sufficient for the combustion of at least 10 g. of steel.

If some undissolved material should be noticed in the bottom of the flask, it is necessary on repeating the experiment to use finer material or to continue the boiling for a longer period. In no case, however, is it permissible to sift a sample of cast iron because the fine powder is likely to contain more graphite than the larger particles. Some kinds of iron alloys will not dissolve in the acid; the carbon in such alloys should not be determined by this method.

Computation.—If p represents the gain in weight of the soda-lime tube (or tubes) in the analysis of a sample weighing s g., then

$$\text{Per cent. C} = \frac{27.3 \times p}{s}$$

Test Analyses. (*a*) *Results of Blank Tests.*—In five experiments, blanks were run for 3 hr. with chrome-sulfuric acid mixture which had been given a preliminary boiling of 1 hr. The first soda-lime tube gained in weight 0.0017, 0.0020, 0.0022, 0.0010 and 0.0030 g. On an average, therefore, the first tube gains 0.0030 g. in weight during 3 hr. boiling. Unless an allowance is made for this, the results obtained in the analysis of a sample of steel weighing 3 g. will be 0.02 per cent. too high.

The above values were all obtained with five different portions of the acid mixture. Using one and the same portion of the acid

and boiling for varying lengths of time, the following changes in weight of the two soda-lime tubes were observed.

TABLE 77

Chrome-sulfuric acid, previously boiled for 1 hr.	Gain in weight in g.	
	Soda-lime, tube 1	Soda-lime, tube 2
Boiled 1 hr. more	0.0009	0.0002
Boiled 2 hr. more	0.0018	0.0005
Boiled 3 hr. more	0.0010	0.0001
Boiled 3 hr. more	0.0016	0.0008
Total gain in 9 hr	0.0053	0.0016

It is evident that the weight changes in the second tube are usually within the experimental error.

(*b*) *Experiments with Pure Sodium Oxalate.*—Sodium oxalate is now being used as a standard in volumetric analysis. It may be used equally well to test the accuracy of a combustion method.

In the following experiments the pure sodium oxalate was weighed into a little glass bucket which was suspended from the hook on the end of the condenser in the Corleis flask. In experiments 9 to 12, water was substituted for the copper sulfate solution and, as expected, this had no appreciable effect on the results in the absence of metal.

TABLE 78

No.	Weight $Na_2C_2O_4$ in g.	Calculated weight of CO_2	Observed gains in weight		Increase over calculated weight	
			Tube 1	Tube 2	Tube 1	Tube 2
1	0.1045	0.0686	0.0707	0.0010	0.0021	0.0010
2	0.1000	0.0657	0.0660	.....	0.0003	.....
3	0.2000	0.1313	0.1325	.....	0.0012	.....
4	0.2000	0.1313	0.1328	0.0013	0.0015	0.0013
5	0.3000	0.1970	0.1997	0.0008	0.0027	0.0008
6	0.3000	0.1970	0.1755	0.0223	.....	0.0008
7	0.3954	0.2597	0.2418	0.0205	.....	0.0026
8	0.4047	0.2658	0.2651	0.0016	.....	0.0009
9	0.1000	0.0657	0.0671	.....	0.0014	.....
10	0.1000	0.0657	0.0683	.....	0.0026	.....
11	0.1000	0.0657	0.0673	.....	0.0016	.....
12	0.3000	0.1970	0.1975	0.0004	0.0005	0.0004

The experimental results shown in Table 78 justify the following conclusions:

1. The slight gains in weight in the second tube need not be considered in calculating the carbon content except in those cases (Exp. 6 to 8) in which the contents of the first tube have become so far exhausted that it is no longer able to retain all the carbon dioxide.

2. If the first tube is not exhausted, all of the carbon dioxide is absorbed by it; the gain in weight of the first tube is then slightly greater than corresponds to the theoretical quantity of carbon dioxide. Since the sodium oxalate sample was known to be pure, the trouble cannot be traced to the sample. Aside from possible errors in weighing, the average of many determinations made at different times corresponds to an excess weight of about 0.002 g., or practically the same as was obtained in the blank run.

It may be assumed, then, that the weight of carbon dioxide found in the combustion of iron or steel will usually be a few hundredths of 1 per cent. higher by the chrome-sulfuric acid method than by other combustion methods, unless a correction for the blank is made. Assuming an average excess weight of 0.002 g. the error will amount to:

0.05 per cent. with a sample weighing 1 g.
0.02 per cent. with a sample weighing 2 g.
0.01 per cent. with a sample weighing 5 g.
(See also the carbon values in Table 79)

(*c*) *Experiments with Different Kinds of Material.*—The results of a number of determinations are shown in Table 79 on page 138.

NOTES.—In experiments *a* and *b* of sample 4 the shavings made by planing were boiled for 4 hr. with the chrome-sulfuric acid mixture. At the end of the run it was found that some unattacked material was left, especially in experiment *a*. The determinations were therefore repeated after the sample had been more finely divided by hammering and cutting. After boiling for 4–½ hr. nothing remained but transparent flocks of gelatinous silica having the form of the original sample.

In sample 5 (chrome-tungsten steel in the form of fine turnings) large quantities of yellow tungstic acid separated during the boiling and caused a violent bumping of the solution. No undecomposed material was found after 4 hr. heating.

TABLE 79

No.	Material	Exp. No.	Weight in gr.	Gain in weight		Per cent. carbon	Per cent. C after deducting 0.002 g. from weight
				Tube 1	Tube 2		
1	Soft ingot iron	*a*	4.000	0.0093	[0.0007]	0.06	0.05
		b	4.000	0.0085	[0.0009]	0.06	0.04
2	High carbon steel	*a*	3.000	0.1422	[0]	1.29	1.27
		b	3.000	0.1420	[0]	1.29	1.27
3	Nickel steel with 24 per cent. nickel	*a*	3.000	0.0820	[0.0012]	0.75	0.73
		b	3.000	0.0845	[0.0015]	0.77	0.75
4	Silicon steel with 1.65 per cent. silicon	*a*	3.000	0.0720	0.0003	0.65	0.64
		b	3.000	0.0832	[0.006]	0.76	0.74
		c	3.000	0.0843	[0]	0.77	0.75
		d	3.000	0.0845	[0.0003]	0.77	0.75
5	Chrome-tungsten steel with high tungsten	*a*	3.000	0.0889	[0.0008]	0.81	0.79
		b	3.000	0.0898	[0.0011]	0.82	0.80
6	Gray cast iron	*a*	1.000	0.1563	[0.0011]	4.26	4.21
		b	1.000	0.1570	[0.0006]	4.28	4.23

ACCURACY OF THE VALUES FOUND BY THE CHROME-SULFURIC ACID METHOD

Allowing for differences in the composition of the samples, as discussed in Part I of this book, the errors which may occur in the chrome-sulfuric acid method are traceable chiefly to errors in weighing and to the gain in weight of the soda-lime tube from some source other than the carbon in the sample.

Assuming that the errors of weighing are not greater than ± 0.001 g. and that the first soda-lime tube has an average weight of 0.002 g. too high (see the results of the blank and the experiments with sodium oxalate) the total error in a properly-conducted analysis probably lies between $+0.001$ to $+0.003$ g. carbon dioxide.

The error in all cases would be found in the second decimal place of the calculated percentage and would be, for example, be-

tween 0.01 and 0.03 per cent. with a 3 g. sample or between 0.005 and 0.02 per cent. with a 5 g. sample.

It follows from this that the carbon content is uncertain in the second decimal and it is sometimes customary, for this reason, to write the second figure small.

The use of a third decimal, except in such cases where very unusual precautions have been taken, is not only unnecessary but also shows that the analyst is ignorant of the probable error of the method.

If the carbon determination is carefully carried out, the following values may be taken as permissible variations in the analysis of samples weighing about 3 g.

With a carbon content		Greatest allowable deviation
from	to	
0.02	0.15 per cent.	± 0.005 per cent.
0.15	1.00 per cent.	± 0.01 per cent.
1.00	2.00 per cent.	± 0.02 per cent.
2.00 and higher per cent.		± 0.03 per cent.

Greater accuracy, as for example, that given by Bischoff[1] for low carbon material, can scarcely be attained.

Applicability of the Chrome-sulfuric Acid Process

The chrome-sulfuric acid method is suitable for all sorts of irons, steels and special steels as well as for numerous other metals and alloys used in the steel industry. The following substances can be decomposed without leaving a residue; ferro-manganese, chrome-manganese, ferro-vanadium, ferro-molybdenum, ferro-titanium, manganese-titanium, ferro-boron, metallic nickel and metallic molybdenum in the form of fine powder. The method cannot be used for the following materials which are scarcely attacked after 4 hr. treatment; ferro-silicon, ferro-tungsten, metallic tungsten, ferro-phosphorus, ferro-chromium, and metallic molybdenum either as wire or as sheet.

[1] Stahl u. Eisen, **22**, 727.

2. DETERMINATION OF CARBON IN THE DRY WAY BY DIRECT COMBUSTION IN OXYGEN

(COMBUSTION IN AN ELECTRICALLY HEATED TUBE FURNACE)

Principle.—On heating iron and steel to about 1100° or 1200° in a current of oxygen, the metal is oxidized completely to ferric oxide and any other elements that may be present are also changed to oxides. Of these latter elements carbon and sulfur form volatile compounds which can be absorbed and determined. With excess of oxygen, carbon forms carbon dioxide and sulfur either the dioxide or the trioxide.

If the evolved gases were absorbed directly in a soda-lime tube and the carbon content calculated from the gain in weight, the results might be too high, due to the sulfur present, or too low because of insufficient oxidation (formation of carbon monoxide).

In order to determine carbon accurately, therefore, the gases must be freed from oxides of sulfur by suitable means and any carbon monoxide must be oxidized to dioxide before the absorption train is reached.[1]

Apparatus.—For heating the porcelain or quartz tube in which the combustion takes place, a horizontal tube furnace with variable resistances and connection with a high-tension electric circuit is desirable.

If many carbon determinations are to be made a tube furnace of large diameter is recommended; several porcelain tubes can be heated in it at the same time and with the use of only a little more current. A platinum, platinum-rhodium thermoelement with a millivoltmeter is used to measure the temperature[2] in the furnace.[3]

[1] See Müller and Diethelm, Z. angew. Chem., **23**, 2114 (1910).

[2] For further details consult Le Chatelier's "High-temperature Measurements" (Boudouard-Burgess).

[3] The cost of equipping an apparatus for combustion in the electric tube furnace is shown approximately in the following table taken from the catalog of Heraeus of Hanau, Germany.

1 Horizontal tube furnace 50 mm. wide, 30 cm. long, about	$20.00
Platinum necessary (about 10 g.), about	$17.50
1 Adjustable resistance box, about	$20.00
1 Thermoelement with protecting tube, about	$15.00
1 Siemans-Halske galvanometer, about	$40.00

This furnace will give temperatures from 1100° to 1200° with about 10 amp. of current at 220 volts.

To avoid overloading the furnace at the beginning of the heating it is best to have an ammeter in the circuit.

The combustion itself takes place in a tube made of quartz or glazed porcelain. The tube contains a little coarse copper oxide and some chromate mixture. To prepare the latter, mix together 9 parts of potassium chromate with 1 part of potassium dichromate, heat till sintered in a porcelain crucible and grind the sintered mass to a coarse powder. This charge would at once melt and lose its efficiency if placed in the hottest part of the tube;

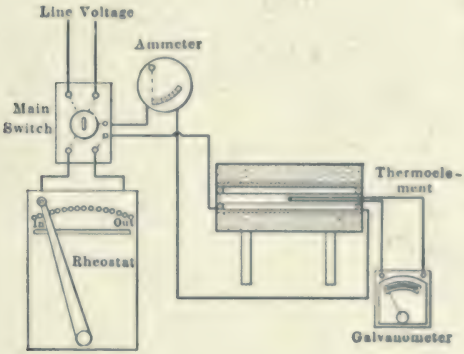

FIG. 112.

in the part that projects from the furnace it is heated by radiation sufficiently to effect the conversion of any carbon monoxide to dioxide and of any sulfur dioxide to sulfuric acid anhydride which is retained by the chromate mixture.

Place a loose plug of ignited asbestos just at the end of the part of the tube that is inside the furnace, after this a layer of copper oxide about 2 cm. long and then an equally long layer of chromate mixture, also between asbestos plugs. The copper oxide is less fusible than the chromate mixture. If, however, it reaches the hot part of the tube and melts, the tube is likely to crack on cooling.

A sketch showing the connections for the tube furnace and for the thermoelement is given in Fig. 112.

The arrangement of the entire apparatus is shown in Fig. 113.

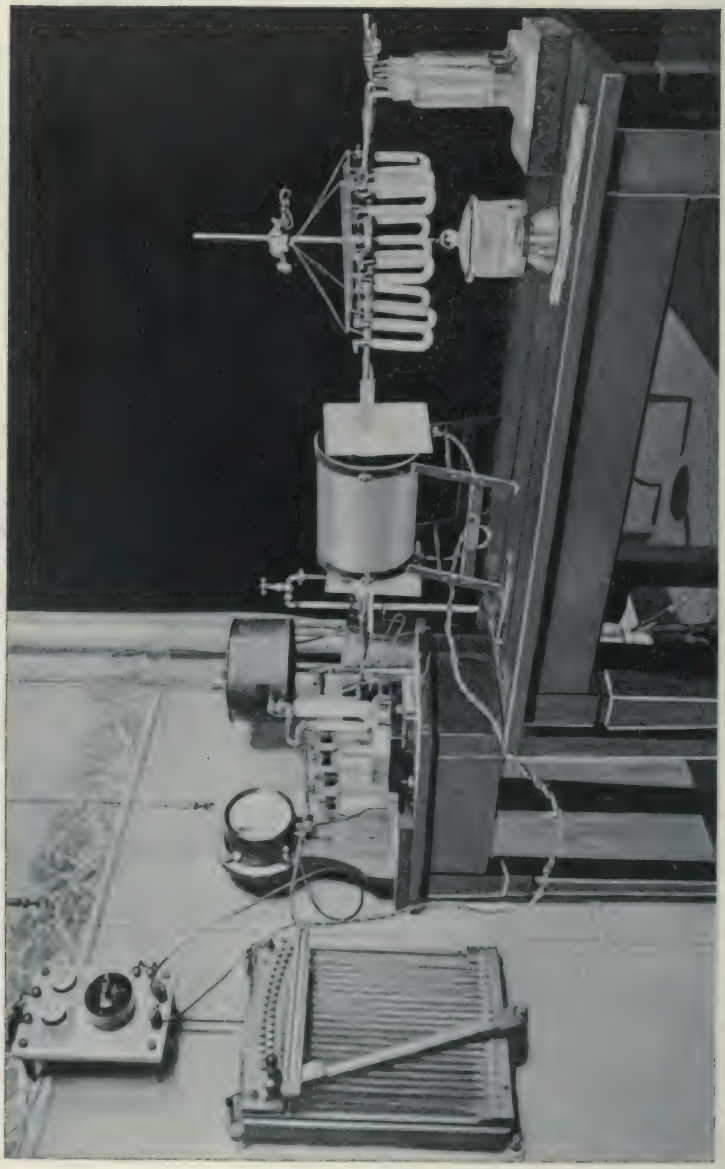

FIG. 113.—Apparatus for carbon determination with an electric furnace.

Its different parts will be described in succession and in the direction of the current of oxygen.[1]

The oxygen is kept in a gasometer filled from a tank of compressed gas. In order to purify the oxygen from the gasometer it passes first through several wash bottles containing concentrated caustic potash solution (1 : 1) then through a large soda-lime tube and finally through a tube containing calcium chloride (or phosphorus pentoxide). A piece of rubber tubing closed with a pinch-cock leads from the last drying-tube to the combustion tube or, in case several tubes are used in one furnace, this rubber tubing leads to a forked glass tube and from there to the different porcelain tubes. The porcelain tubes and the thermoelement in its protecting tube are held firmly in the openings of the furnace with the aid of asbestos wool; take care that the tubes do not come in direct contact with one another or with the walls of the furnace. A good method of keeping the tubes apart is to use a thick piece of asbestos board with holes corresponding to the number of tubes used and through which the tubes will project from both ends of the furnace.

The thermoelement should extend far enough into the furnace so that its junction will be in the hottest part of the tube. The wires of the thermoelement are connected with the poles of the galvanometer and by closing the switch in the main circuit it is possible to tell whether the connections are correctly made. The pointer should move toward the scale. Place the porcelain tubes, filled with copper oxide and the chromate mixture, in the furnace with the filled parts at the front ends, farthest away from the oxygen tank, so that the oxygen passes first through the empty part of the tube, in which the combustion boat is to be placed, then through the copper oxide and chromate mixture, and finally into the absorption train. The first tube in the train contains calcium chloride (or phosphorus pentoxide) to absorb moisture from the gases and the two tubes following are filled with soda-lime and calcium chloride (or phosphorus pentoxide) to absorb carbon dioxide. These tubes are filled and handled exactly as in the chrome-sulfuric acid method (p. 130). Attach a safety tube

[1] The end at which the gas leaves the apparatus is usually called the front end of a combustion train. The train will be described from back to front.

of concentrated sulfuric acid to the last soda-lime tube, to prevent any moisture from getting back into the tube in case the gases should suck back. This tube also serves to indicate the rate at which the gases are passing.

Porcelain tubes, glazed on the outside only, or quartz tubes, may be used for the combustions. If the furnace is 30 cm. long, tubes of 50-cm. length are used. A furnace with an internal diameter of 50 mm. will hold a thermoelement and three combustion tubes of 12 mm. outside diameter.

The porcelain boats used in the combustion for holding the sample should preferably be of unglazed material. To avoid any possible fusing of the boat to the inner wall of the tube, even when boats glazed on the outside are used, it is a good plan to wind pieces of asbestos fiber around the boat about 1 cm. from each end. When the boat is introduced into the tube these fibers prevent it from coming in direct contact with the tube walls.

Procedure.—After weighing the soda-lime tubes, using the precautions described in the chrome-sulfuric acid method, weigh the sample into a boat which has been previously wound with asbestos fibers and ignited. For iron and steel samples with high-carbon content, a weight of 1 g. is usually sufficient and this can be spread on a boat 7 cm. long, 8 mm. wide and 5 mm. deep. For weighing larger samples (2 or 3 g.) which are necessary with low-carbon material, boats about 13 cm. long, 7 mm. wide and 6 mm. deep should be used. Take care in filling the boat not to let pieces of the sample project over the edge, as the molten oxide formed during the combustion will then drop off and come in contact with the inside of the tube. The very coarse shavings which sometimes form in taking the sample cannot be used on this account and must be brought into a denser and flatter form by hammering in a diamond mortar.

It is best not to have the sample too fine. Fine shavings and powder burn very easily, to be sure, but the combustion starts so quickly and proceeds so rapidly that there is danger of there being an insufficient oxygen supply (formation of carbon monoxide) and there is also danger of the liquid in the last flask sucking back, unless the rate of flow of the oxygen is increased quickly. The combustion goes less violently but completely with coarse shavings or thick pieces. Pig iron chips, 2 mm. thick, will burn

readily in the electric furnace, whereas pieces of the same size will be attacked scarcely at all by 4 hr. treatment with the chrome-sulfuric acid mixture.

While the soda-lime tubes and the sample are being weighed, pass a slow current of oxygen through the previously ignited porcelain (or quartz) tube. Connect the closed soda-lime tubes in place, push the boat with the sample to the center of the tube by means of a suitably bent wire or a glass rod, stopper the tube and make a test to see if the apparatus is tight. For this purpose first open the stopcock next to the furnace and allow oxygen to pass into the apparatus until no more bubbles pass through the wash bottle from the gasometer. If the apparatus is found to be tight up to this point, open the next stopcocks in the tubes of the train, one by one, waiting each time until the gas bubbles stop. Then, if the connections are all tight, relieve the excess oxygen pressure by opening gradually the stopcock in the front end of the train. Continue passing a slow stream of oxygen through the apparatus and begin the heating.

In working with a Heraeus furnace of 50-mm. internal diameter, with which the maximum temperature of 1300° is given with a current of 10.5 amperes at 220 volts, the method of operation is as follows:

First, have all the resistance in the electric circuit. Turn on the current and move the rheostat arm back until the ammeter shows 9 amperes. As the current drops 1 or 2 amperes cut out more resistance and keep the current at 9 to 10 amperes.

During a combustion the galvanometer indicates approximately these changes in temperature:

after 5 minutes, 200° C.
after 15 minutes, 650° C.
after 30 minutes, 850° C.
after 45 minutes, 980° C.
after 60 minutes, 1060° C.
after 67 minutes, 1100° C.

The combustion usually starts at a temperature between 850° and 980° and is indicated by a sudden slowing up of the gas current in the last wash bottle and an increase in the rate at which the oxygen flows through the first wash bottle. To prevent the back

pressure from forcing air into the soda-lime tubes, increase the supply of oxygen while the sample is burning.

Maintain the temperature of the furnace for 15 or 20 min. at 1100° or, at the most, 1200°, and continue passing a slow stream of oxygen through the apparatus.

At the end of this time the combustion is surely ended. Shut off the electric current, turn the lever of the resistance box back and pass oxygen through the tube for 15 min. longer, to drive all of the carbon dioxide out of the combustion tube and drying tube. Finally, close the stopcocks of the soda-lime tubes, remove them from the train and weigh them after allowing them to stand at least half an hour in the balance case.[1] After the soda-lime tubes have been taken off, close the stopcock from the oxygen tank and allow the furnace to cool.

If another combustion is to be made at once, weigh out the new sample while the furnace is cooling. When the temperature has fallen to about 600° or less, pull out the old boat with a hook made of clean copper wire. Pass oxygen through the tube for 5 min., connect the weighed soda-lime tubes and push the new sample into the tube. Turn on the electric current and proceed as before. The time taken to bring the warm tube up to the combustion temperature is much less now and less current is used, two factors of great importance where work is being done on a large scale. If large pieces are used for combustion it often happens that the ferric oxide after the combustion is left in the form of loose pieces which can easily be removed from the boat; if the material is finely divided the mass usually fuses to the boat.

The porcelain boat can be cleaned for use a second time by heating it for a long time with concentrated hydrochloric acid to remove the adhering oxide. This hardly pays, however, at the present price of unglazed porcelain.

The computation of the carbon content is the same as in the previous method.

[1] This leaves oxygen in the tubes which weighs slightly more than the air they originally contained. The tubes are so small, and there is so little free air space that it is not necessary to correct for this slight error. If the initial weight of the tubes was made when they were filled with oxygen, this error disappears.

Test Analyses.—(*a*) *Blank Runs.*—Weight changes in the soda-lime tubes in carrying out the blanks (running oxygen through the tubes as in an actual analysis) are sometimes negative and sometimes positive. Usually they do not amount to more than −0.0005 g. They are smaller than the blanks in the chrome-sulfuric acid method and are within the limits of accuracy of the weighings.

(*b*) *Results with Different Materials.*—In Table 80 are given the results of some analyses by this method compared with values obtained by the chrome-sulfuric acid results.

TABLE 80.—CARBON DETERMINED BY COMBUSTION IN OXYGEN

No.	Material	Exp. No.	Weight of sample in g.	Gain in weight		Per cent. C.	Per cent. C chrome-sulfuric acid method[3]
				Tube 1	Tube 2		
1	Mild steel....	(*a*)	2.773	0.0056	0.0015	0.06	0.06
		(*b*)	2.001	0.0034	0.0008	0.05	
2	Medium carbon steel.	(*a*)	1.9475	0.0386	.....	0.54	0.53
		(*b*)	2.0971	0.0398	.....	0.52	
3	High carbon steel.	(*a*)	2.0006	0.0948	.....	1.29[1]	1.29
		(*b*)	2.0044	0.0949	.....	1.29	
4	Pig iron as fine turnings.	(*a*)	1.0023	0.1137	0.0006	3.09	3.14
		(*b*)	1.0053	0.1145	0.0003	3.10	
5	Cast iron, pieces 2 mm. in thickness.	(*a*)	0.9970	0.1285	.....	3.52	3.59[2]
		(*b*)	1.0019	0.1295	.....	3.53	

1. After the combustion of sample 3, the two samples were weighed again and showed the following gain in weight due to the formation of oxide:

(*a*) gained 0.8169 g.
(*b*) gained 0.8128 g.

These values indicate that the relation Fe : O is approximately 2 : 3 so that it is chiefly Fe_2O_3 which is formed by the combustion.

2. Sample 5 was used in the form of fine turnings for the chrome-sulfuric acid method.

3. The carbon values given in the last column as the results of the chrome-

sulfuric acid method are not corrected. If the weight 0.002 g. is subtracted from the actual gain in weight of the soda lime tube (*cf.* p. 137) the agreement between the results by the two methods is even better.

Accuracy of the Values Found by the Direct Combustion Method

The weight changes in the soda-lime tubes in the blank runs are within the error of weighing. Assuming the error of weighing to be not greater than ± 0.0005 g., the percentage errors are:

For a 1-g. sample $\pm$ 0.015 per cent.
For a 2-g. sample $\pm$ 0.007 per cent.

The method of direct combustion in oxygen is, therefore, slightly more exact than the chrome-sulfuric acid method. In this case, too, the errors are found in the second decimal place so that if small weight samples are taken (1 to 3 g.) the allowable deviations are the same as those given for the chrome-sulfuric acid method (p. 138).

In order to reduce the effect of the weighing error and so get more accurate carbon values, a larger sample may be taken (10 to 15 g.) and burned in a larger porcelain boat and in a large tube.

Applicability of the Method

All the metals and alloys mentioned under the chrome-sulfuric acid method, including those which could not be decomposed by that method, will be decomposed in a current of oxygen at temperatures between 1100° to 1200°.

With certain substances, like ferro-vanadium and molybdenum which give readily fusible oxides that are likely to injure the combustion tube, it is advisable to place the sample in the boat on top of some absorbent material such as ignited alumina.

3. DETERMINATION OF CARBON IN LOW-CARBON MATERIALS (BARIUM HYDROXIDE METHOD)

As will be noticed in the results of the carbon determinations made by the two preceding methods, the values are not very exact if the percentage of carbon is very low (Tables 79 and 80)

because, on the one hand, it is difficult to reduce the sources of error and, on the other hand, the original sample cannot weigh much more than 2 or 3 g. without greatly increasing the analytical difficulties.

The accuracy of the carbon determination can be increased, however, if the carbon is weighed not as carbon dioxide with low molecular weight but in the form of a compound with high molecular weight.

Principle.—The carbon dioxide formed by the combustion of the carbon is absorbed by barium hydroxide and changed to barium carbonate which is filtered off, dissolved in hydrochloric acid, the barium precipitated by dilute sulfuric acid, and the resulting barium sulfate weighed. One molecule of barium sulfate is formed, therefore, for each atom of carbon originally present.

The principle of the method involves nothing new; changing the carbon dioxide to barium carbonate was recommended by O. Petterson and Smitt[1] and also by Aupperle[2] for the determination of carbon in iron and steel.

The directions given here, however, suggest a better way than has hitherto been proposed for preventing the absorption of carbon dioxide from the air.

Necessary Apparatus and Solutions.—The sample is burned in a tube heated by an electric furnace exactly as described in the previous method. Instead of using soda-lime tubes for the absorption of the carbon dioxide, a bubble tube containing barium hydroxide is connected directly to the combustion tube.[3] This leads into a flask of barium hydroxide which is protected from the carbon dioxide of the air by a soda-lime tube. (See Fig. 114.)

For filtering and washing the barium carbonate which precipitates in the bubble tube, without fear of contamination by the carbon dioxide of the air, the arrangement shown in Fig. 115 is used, consisting of a suction bottle, tube-funnel, several soda-lime tubes, etc.

The barium carbonate precipitate must be washed with water that is free from carbonic acid. This is made by boiling distilled water and allowing it to cool in an atmosphere free from carbon

[1] Ber. **23,** 1401 and Z. anal. Chem., **32,** 385.

[2] J. Am. Chem. Soc., **28,** 858 and Chem. Ztg. Rep., **1906,** 316.

[3] It is unnecessary to remove the moisture from the escaping gases.

dioxide. This water is stored in a large bottle provided with a siphon and a soda-lime tube. (Upper bottle in Fig. 115.) The barium hydroxide solution used in the analysis is prepared as follows:

Dissolve 194 g. of crystallized barium chloride in a 5-liter bottle and mix it with an aqueous solution of 64 g. caustic soda. Fill the bottle with water and shake thoroughly. After the small precipitate of barium carbonate has settled out, and the supernatant liquid is clear, attach the emptying device shown in Fig. 114*a*. The stopcock on the siphon tube should be protected by a rubber stopper when not in use, so that it will not become plugged with barium carbonate.

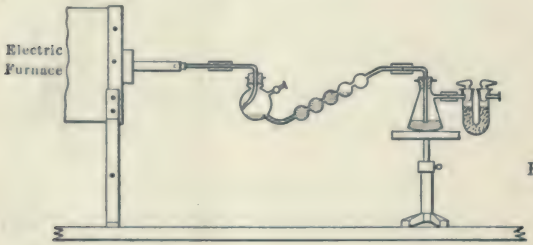

FIG. 114.

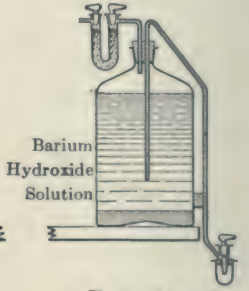

FIG. 114*a*.

Procedure.—Weigh out 2 g. of the sample into a porcelain boat and place the boat in the combustion tube of the electric furnace. Connect the combustion tube with the train shown in Fig. 114, consisting of a dry, empty bubble tube, a dry, empty wash bottle, and a *U*-tube filled with soda-lime. To free the entire apparatus from carbon dioxide, pass a current of purified oxygen through the entire apparatus for 20 min. At the end of this time, disconnect the wash bottle from the bubble tube, without interrupting the current of oxygen, fill the bottle with clear barium hydroxide solution and at once connect it again to the bubble tube. If after oxygen has passed for about 15 min. longer, the wash bottle shows no turbidity, indicating that the apparatus is free from carbon dioxide, introduce enough barium hydroxide into the bubble tube so that when the oxygen is passing the solution will not reach beyond the next to last bulb of the tube. Then replace this absorption tube in the train between the

porcelain tube and the wash bottle. Take care in filling the bubble tube to avoid the entrance of air containing carbon dioxide.

The apparatus must be tested to see that it is tight before the combustion is started. To make the test, close the stopcock in the soda-lime tube and allow oxygen to enter the train. If the apparatus is tight the flow of gas soon stops. If the connections are thus shown to be tight, relieve the oxygen pressure by opening the stopcock slowly. Then turn on the electric current and start the combustion exactly as in the previous method (*cf.* p. 145).[1]

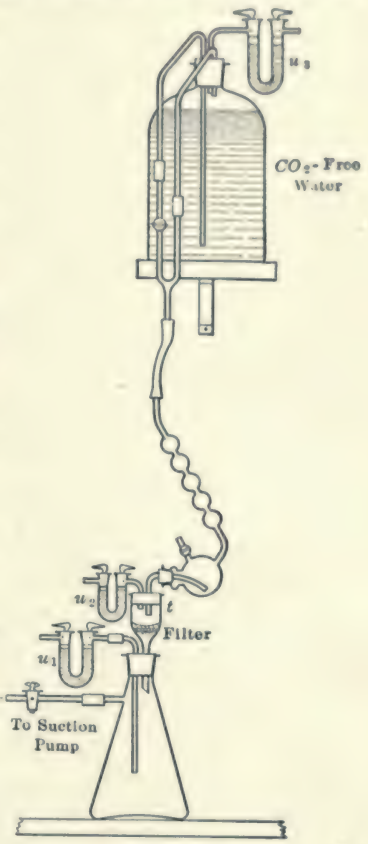

FIG. 115.

The filtering arrangement used for the barium carbonate can be set up as shown in Fig. 115 while the combustion is taking place. Place a little glass wool in the funnel t and on it place a porcelain filter-plate having the same diameter as the tube and covered with a piece of filter paper cut to fit. Cover this filter with dry, purified asbestos, like that used in filtering graphite (p. 166) spreading it out, by means of a wash bottle and the suction pump, to form a fairly thick, uniform layer.

After preparing the funnel in this way, insert it into one hole of a doubly perforated rubber stopper in a suction bottle. Through the other hole insert a glass tube and connect this with a well-filled soda-lime tube, U_1. Attach a glass stopcock to the suction

[1] It will be noticed in most cases that the barium hydroxide solution begins to grow turbid when the furnace is heated to about 700° C., showing that the carbon starts burning before much of the iron is oxidized.

bottle and connect this, through a wash bottle containing a little water, to the suction pump. Fit a two-holed rubber stopper to the filter funnel, t, connect it through one hole with the soda-lime tube, u_2, and close the other hole temporarily with a piece of glass stirring rod. To remove carbon dioxide from the filtering apparatus, apply suction and draw a slow stream of air through the tube u_2 for some time and then through the tube u_1. When this is accomplished, close the stopcock leading to the pump and turn off the suction.

After finishing the combustion, which will not require more than an hour in most cases, disconnect the bubble tube from the train and take away the wash bottle which was attached to it. Remove the glass plug from the stopper in the funnel, t, in Fig. 115, and insert in its place the extension tube of the bubble tube. Connect the free end of the latter by rubber tubing with the forked tube extending from a large bottle of water, free from carbon dioxide, which should be supported about 100 to 120 cm. above the top of the working bench.

Close the stopcocks of the two soda-lime tubes u_1 and u_2, start the suction pump and, by opening the cock between the pump and the wash flask, apply gentle suction to the apparatus. The rate of flow can be determined by watching the bubbles in the wash-bottle (not shown in the drawing).

The barium hydroxide solution and the flocculent barium carbonate precipitate from the bubble tube are thus siphoned into the funnel and filtration takes place while carbon dioxide free air is supplied through the soda-lime tube u_3. When all the liquid has passed through the filter, open the stopcock in the siphon tube leading from the large water-bottle (the stopcocks on the large soda-lime tube u_3 are kept open all the time) and allow water to flow into the bubble tube. While the water is passing through, shake the bubble tube to remove any deposit of barium carbonate from the glass sides of the tube. Close the stopcock on the siphon and allow all the liquid to filter off with a constant, slow suction from the pump. Wash the bubble tube several times in this way. To get enough water in the large bulb of the bubble tube, the stopcock on the bulb may be opened for a short time to allow air to escape. After about six washings, the bubble tube, filter and precipitate are free from barium hydroxide. Then disconnect the

bubble tube and the funnel from the apparatus, dissolve the barium carbonate precipitate on the filter in dilute hydrochloric acid and allow the acid to run into a small beaker. Wash the bubble tube and the inlet tube several times with dilute hydrochloric acid and water and allow the washings to run through the funnel into the major portion of the solution. Finally, wash the filter thoroughly with dilute hydrochloric acid and water. Evaporate the resulting solution on the water bath to about 10 cc. and transfer it to a weighed porcelain crucible. Rinse out the beaker with a little dilute hydrochloric acid, add a few drops of dilute sulfuric acid to the solution in the crucible, and thus convert the barium into barium sulfate. Evaporate the solution to dryness in the crucible and gradually raise the temperature until the excess of sulfuric acid has been expelled. Finally heat the crucible to redness over the full flame of the Bunsen burner, cool the crucible at least half an hour in a desiccator, and weigh.

Instead of evaporating the barium chloride solution in the crucible, the concentrated, slightly acid solution may be treated with a slight excess of dilute sulfuric acid, the precipitated barium sulfate allowed to settle, and filtered after the solution has become clear. The precipitate can be ignited and weighed in a platinum or porcelain crucible, or a Gooch crucible may be used (*cf.* p. 193).

Computation.—Since each atom of carbon forms one molecule of barium carbonate which is equivalent to one molecule of barium sulfate, the percentage of carbon in a sample which weighed s g. and gave p g. of barium sulfate, is

$$\text{Per cent. C.} = \frac{5.14\,p}{s}$$

Test Analyses.—(*a*) *Blank Runs.*—Blank runs were made exactly as described above without introducing the sample. The tube was heated and the oxygen passed through the absorption tube containing barium hydroxide. At the end of the run the barium hydroxide showed only a slight turbidity due to barium carbonate. The solution was filtered, the carbonate changed to sulfate and weighed as such.

The values obtained were:

Exp. 1 = 0.0010 g. $BaSO_4$
Exp. 2 = 0.0012 g. $BaSO_4$

(*b*) *Analysis of Various Materials.*—For purposes of comparison the values found by this method are given in Table 81 with the values found by the two other methods.

TABLE 81

Number	Kind of material	Combustion in oxygen in electric furnace						Chrome sulfuric acid method[2]
		Barium hydroxide method			Absorption of CO_2 in soda lime			
		Weight sample	Weight $BaSO_4$	Per cent. C	Weight sample	Weight CO_2	Per cent. C	Per cent. C
1	Special steel (contained Cr, W and V).	0.9997 0.9996	0.1151 0.1151	0.592 0.592	2.210	0.0486	0.60	0.62
2	Metallic nickel.*	1.5064 1.0033	0.0567 0.0390	0.193 0.200	1.0085 1.0060	0.0073 0.0074	0.20 0.20	0.22
3	Ordinary steel.	1.0150 1.0045	1.1307 0.1295	0.662 0.662	1.674 1.713	0.0401 0.0413	0.65 0.66	0.66
4	Boiler plate.	2.534 2.517	0.0221 0.0219	0.045 0.045	2.399	0.0046	0.05	0.05
5	Ingot iron...	3.015 2.502	0.0294 0.0226	0.050 0.046	2.773 2.001	0.0056 0.0034	0.06 0.05	0.06
6	Silico-manganese.	1.191 1.807	0.0122 0.0183	0.053 0.052	1.104	0.0037	0.09	*
7	Ingot iron...	2.50 2.50	0.0069 0.0070	0.014 0.014	1.996	0.0014	0.02	0.02
8	Tungsten....	1.001 1.007	0.0035 0.0032	0.018 0.016	1.327 1.002	0.0013 0.0016	0.03 0.04	*
9	Ingot iron...	2.536 2.688	0.0059 0.0057	0.012 0.011	2.681 2.660	0.0019 0.0016	0.02 0.02	0.02

* Not attacked.

1. Metallic nickel does not burn completely at 1200°. The turnings become coated with a layer of oxide which does not melt at that temperature but in spite of this fact the carbon seems to burn as is indicated by the agreement between the three sets of values.

2. The values given under the chrome-sulfuric acid method are uncorrected (*cf.* p. 135 and p. 147, Note 3).

Accuracy of the Carbon Values Found by the Barium Hydroxide Method

The errors in weighing a barium sulfate precipitate are slight if care is taken, so that the values for carbon found by the barium hydroxide method with a 2-g. sample and low-carbon content are probably correct within 0.003 per cent. Duplicate determinations should not differ by more than

± 0.002 per cent. for a carbon content between 0.010 and 0.25 per cent.
or
± 0.004 per cent. for a carbon content between 0.25 and 0.60 per cent.

Applicability of the Barium Hydroxide Method

The method is good for all low-carbon material which can be burned in the electric furnace with oxygen at temperatures not above 1200°. If the carbon content is greater than 0.60 per cent., the quantity of barium sulfate formed is so large that a small original sample must be used. Since, however, it is difficult to get representative samples of very small weight, it is better to use Method 1 or Method 2 for the higher carbon steels.

4. DETERMINATION OF TOTAL CARBON BY THE POTASSIUM-CUPRIC-CHLORIDE METHOD

A number of methods have been worked out for the removal of nearly all the iron before attempting to determine the total carbon content of a sample of iron or steel. Thus Wöhler volatilized the iron as ferric chloride by heating the sample in an atmosphere of chlorine. Another method consists in dissolving out the iron by means of a solution containing a copper salt in the presence of either ammonium chloride (Berzelius) or potassium chloride (Richter) to prevent the precipitation of cuprous chloride. Potassium chloride is preferred because ammonium chloride is likely to be contaminated with pyridine chloride, which itself contains carbon. Cupric chloride and potassium chloride crystallize together in the form of a double salt corre-

sponding to the symbol, $2KCl.CuCl_2.2H_2O$., and this salt is often given the trivial name "double chloride" by chemists engaged in the analysis of steel. The double chloride method was until recently considered the most reliable method for determining the total carbon in iron and steel. It has been shown, however, that certain alloy steels, especially chrome-tungsten steel, give unreliable results by it, probably on account of some carbon being lost as hydrocarbon. The method is still used a great deal and gives thoroughly reliable results with most materials.

After the removal of the iron, the carbon can be determined by combustion either in an electric or gas-heated furnace. Inasmuch as many laboratories are not equipped with electric furnaces, especially those laboratories which use the double chloride method, the procedure will be described as carried out with a gas-heated furnace.

Principle.—When metallic iron is placed in contact with a solution of a cupric salt, the iron, because of its greater solution tension replaces the copper which is precipitated upon the remaining iron. In the presence of an excess of cupric salt, the deposited copper reacts to form cuprous chloride which is kept in solution by the potassium chloride, and to some extent by the hydrochloric acid, with which it forms a soluble double salt. The reactions may be expressed as follows:

$$Fe + CuCl_2 = FeCl_2 + Cu$$
$$Cu + 2CuCl_2 = Cu_2Cl_2$$

or

$$Fe + Cu^{++} = Fe^{++} + Cu$$
$$Cu + Cu^{++} = 2Cu^{+}$$

Since hydrochloric acid reacts with iron carbide and with its solid solution in iron, setting free gaseous hydrocarbons, it was at first thought necessary to carry out the treatment with potassium cupric chloride in a perfectly neutral solution but it was found later that no hydrocarbons were set free by dilute hydrochloric acid in the presence of a cupric salt and that, in fact, the presence of nearly 10 per cent. by volume of strong hydrochloric acid is not only permissible but beneficial; in many cases the results are higher and nearer the truth.

Necessary Apparatus and Solutions.—The combustion train, Fig. 116, consists first of a short preheating furnace containing a glazed porcelain tube filled with granular cupric oxide between loose plugs of ignited asbestos. This serves to oxidize any gaseous carbon compounds that may possibly be present in the oxygen supply. Between this furnace, and the longer, ten-burner combustion furnace in which the sample is burned, is a Geissler bulb, with the bottom bulbs about two-thirds filled with strong caustic potash solution (1:1). This serves to remove any carbon dioxide from the oxygen, or air, used in the combustion.

The combustion tube, made of glazed porcelain, contains copper oxide in the end near the absorption train, between plugs

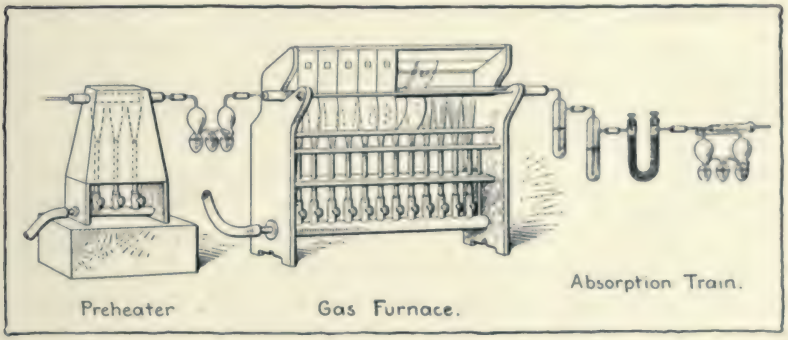

FIG. 116.

of ignited asbestos, but space is left at the other end so that the sample can be introduced into the hottest part of the furnace.

The absorption train consists of a small bubble tube about one-fourth filled with a saturated solution of ferrous sulfate (60 g. $FeSO_4.7H_2O$ in 100 cc. water), a similar tube containing about 10 cc. of a saturated solution of silver sulfate in sulfuric acid (sp. gr. 1.40), a U-tube containing granular calcium chloride (or phosphorus pentoxide) and a Geissler bulb containing caustic potash solution (1 : 2) with a prolong filled with calcium chloride.

The purpose of the ferrous sulfate is to reduce any chlorine that may be evolved during the combustion of the residue obtained after treatment with potassium cupric chloride solution. The ferrous sulfate changes the chlorine to hydrochloric acid

which is retained partly as ferric salt; if any escapes it is caught by the silver sulfate in the next tube.

In filling the calcium chloride tubes, especially the prolong of the Geissler bulb, take care to press down the granular calcium chloride, using particles ⅛ in. in diameter. If the tube is loosely filled some moisture is likely to escape; for this reason a negative blank is often obtained by the beginner.

Instead of the tubes of ferrous sulfate and silver sulfate, the use of anhydrous cupric sulfate followed by anhydrous cuprous chloride has been recommended, or, as suggested by E. S. Johnson, a column of 20-mesh zinc between glass-wool plugs will serve to remove either acid or chlorine.

Instead of the Geissler tube, U-tubes filled with soda-lime and calcium chloride may be used as in Method I, p. 130.

Potassium Cupric Chloride Solution.—Dissolve 300 g. of the double chloride in water containing 75 cc. of concentrated hydrochloric acid (sp. gr. 1.2,) and dilute the solution to 1 liter.

Ignited Asbestos.—Place the asbestos in a dish and heat it to bright redness in a muffle furnace. Remove the dish, allow the asbestos to cool somewhat, and turn over the asbestos. Again heat to redness in the muffle furnace. While cooling, keep the dish covered to prevent dirt from falling into it. If necessary, cut the ignited asbestos into short wads and add enough water to form a fairly thick suspension.

Procedure.—Weigh out 3 g. of ordinary steel, or 1 g. of pig iron, into a 400-cc. beaker and cover the sample with 100 cc. of the double chloride solution for each g. of metal taken. Stir the solution with some form of mechanical stirrer until all the iron has dissolved. It is very easy to tell when the solution is complete by holding the beaker up to the light. If pieces of undissolved metal remain, they will be coated with metallic copper, which is readily distinguished from the black carbonaceous residue.

Prepare an asbestos filter by placing a coil of fairly heavy copper wire in the bottom of a tube funnel, like that shown in Fig. 115, at *t*, and cover this coil with about an inch of wet, ignited asbestos. Filter off the residue from the double chloride treatment and wash out the beaker with 10 cc. of double chloride solution diluted with an equal volume of water. Moderate suc-

tion may be used but this is not necessary. Transfer all of the residue to the filter by means of dilute hydrochloric acid from a wash bottle. Finally wash the residue on the filter with hot water until free from chloride. Carefully push up the filter from the funnel and transfer it, bottom down, to a clean watch-glass. Rub the side of the funnel with ignited asbestos to remove any adhering carbon, and add this to the main portion on the watch-glass. Cover and dry for an hour or two at a temperature between 95° and 100°. It is then ready for the combustion.

In starting with a freshly-filled combustion tube, it should be heated half an hour while passing a current of oxygen through it. Then attach the absorption tube, weighed with the same precautions as described for weighing the soda-lime tubes in Method I, p. 131, and make a blank run to be sure the apparatus is ready for use. Heat the tube red hot and pass oxygen through it for 20 min., at a rate such that two or three bubbles per second pass through the absorption tube, then turn out the burners under the back end of the furnace, where the sample is to be introduced, and pass air through the tube for another 20 min. This may be done either by having an air reservoir under pressure or by applying suction at the front end of the furnace. A simple way of getting suction is to have two large bottles, one on the working bench and the other on the floor. By filling the upper bottle with water and allowing it to siphon slowly into the lower bottle, sufficient suction is obtained. In this way the volume of air passed through the combustion apparatus is shown.

If after the blank run, the absorption tube does not show over 0.0010 g. change in weight, the apparatus is ready for use.

Push the dried asbestos well into the back end of the furnace and wipe out the watch-glass with dry, ignited asbestos. Make sure that the carbon reaches far enough into the tube to get the full heat of the furnace. If the combustion tube is cold, light the preheating furnace and turn on the oxygen, allowing it to pass through the absorption bulb at a maximum rate of three bubbles a second. Light the two forward burners under the combustion tube and gradually turn up the flames until this end of the furnace tube is red hot. Then light the next burner and continue in this way until finally the whole furnace is hot.

To avoid burning the rubber stoppers at the ends of the combustion tube, place shields of heavy asbestos board around each end of the tube where it projects from the furnace and wrap each end near the stopper with a narrow band made of several thicknesses of cheese cloth with the ends dipping in a dish of cold water.

After 20 min. have elapsed from the time the last burner was lighted, stop the current of oxygen and pass a current of air through the tube at the same rate to sweep out all of the carbon dioxide. Gradually turn down the burners under the tube, but if it is to be at once used again for another combustion, it is best to keep the front end hot. Finally detach the Geissler bulb and weigh with the usual precautions.

NOTES.—Instead of oxidizing the residue from the double chloride treatment by a dry combustion, many chemists prefer to oxidize it in the wet way by means of chrome-sulfuric acid, as in Method I, p. 131.

Instead of a combustion tube, the Gooch tubulated crucible or the Shimer crucible may be used. When the combustion is carried out in a crucible, place after the crucible a copper tube about 10 in. long and $\frac{3}{16}$ of an inch inside diameter, with its ends cooled by water jackets. In the center of this tube place a disk of platinum gauze and a 3-in. roll of silver foil, on the side near the crucible, and copper oxide on the other side. Plug the ends of this tube with glass wool and heat it with a burner which is fitted with a flame spreader.

Test Analyses.—To illustrate the accuracy of the above method, the following values are taken quite at random from certificates issued by the Bureau of Standards at Washington, D. C. At the present time most of the analyses made at the Bureau itself are by a direct combustion method.

A sample of pig iron was analyzed by the direct combustion method by five different chemists and the average value obtained was 2.464 per cent. carbon; eight chemists obtained an average value of 2.461 per cent. carbon by the solution and combustion method.

In a sample of Bessemer steel, nine chemists obtained the value 0.805 per cent. carbon by direct combustion and three chemists obtained an average value of 0.806 per cent. carbon by solution and combustion.

With a sample of vanadium steel, eight chemists obtained an

average value of 0.348 per cent. by direct combustion and five chemists obtained an average value of 0.348 per cent. carbon by solution and combustion.

With a sample of nickel steel, seven chemists obtained an average value of 0.375 per cent. carbon by direct combustion and five chemists obtained the average value of 0.379 by solution and combustion.

5. VOLUMETRIC DETERMINATION OF CARBON

Method by J. R. Cain[1]

The difficulty involved in weighing soda-lime tubes or potash bulbs has been mentioned frequently in the literature. The tubes or bulbs are heavy as compared with the weight of carbon to be determined and the variations due to changes in atmospheric conditions are likely to correspond to a considerable fraction of the weight of carbon dioxide absorbed. Thus with a 3-g. sample of steel containing 0.10 per cent. of carbon, the absorbed carbon dioxide will weigh 0.0110 g. An error of 0.0010 g. in the weight of the absorption tube or bulb, and this is by no means unusual, corresponds then to one-eleventh of the total weight of absorbed carbon dioxide. A. A. Blair has even stated that it is almost impossible to get satisfactory results in damp weather, when absorption bulbs are used.

A similar difficulty arose in connection with the determination of carbonic acid in air and in 1861 Pettenkofer[2] proposed the method of absorbing the gas in a measured volume of standard barium hydroxide solution and titrating the excess with standard hydrochloric acid. This method has been adapted to the determination of carbon in iron or steel[3] although it has received little attention in standard text-books on iron and steel analysis.

In 1913, of 62 prominent American laboratories, 32 used the potash bulb, 24 weighed the carbon as barium carbonate, 3 titrated the excess of barium hydroxide as above outlined, 2

[1] J. Ind. Eng. Chem., **6**, 465 (1914).

[2] J. pr. Chem., **82**, 32.

[3] *cf.* McFarlane and Gregory, Chem. News, **94**, 133; Aupperle, J. Am. Chem. Soc., 28, 858.

used soda-lime tubes, and one weighed an absorption tube filled with barium hydroxide.

If, however, the carbon dioxide obtained by combustion of the sample of iron or steel (or of the residue obtained after treatment with potassium cupric chloride) is absorbed in an excess of barium hydroxide solution, the most reliable method is to filter off the precipitated barium carbonate, dissolve it in a measured excess of standard acid, and titrate the excess of the latter with standard alkali. This has the advantage that the analysis is not affected by gases containing sulfur or chlorine which may be formed by the combustion of the metal or of the carbonaceous residue obtained from it by the potassium cupric chloride method. The method is accurate, fairly rapid and specially suitable for the determination of carbon in mild steels or wrought iron.

Apparatus Required.—Any accepted form of combustion apparatus may be used. The oxidation of the carbon may be effected by the chrome-sulfuric acid method, by direct combustion in an electric furnace, or by combustion of the residue obtained after treatment with potassium-cupric chloride. When the combustion takes place in the dry way there is no need of a purifying train in front of the furnace. If it is feared that some finely divided oxide will be carried over, a U-tube filled with 20-mesh quartz, that has been washed with hydrochloric acid and water and dried, may be used.

For absorbing the carbon dioxide, the bubble tube shown in Fig. 114 may be used or the 8-bulb Meyer tube shown in Fig. 117.

For filtering off the barium carbonate the device shown in Fig. 115 or that shown in Fig. 117 (approximately one-tenth the true size is suitable). The use of the latter will be described below.

Solutions Required.—*Tenth-normal Hydrochloric Acid.*—This may be standardized against pure sodium oxalate (Sörensen),[1] against pure sodium carbonate (Gay-Lussac),[2] or by weighing the silver chloride precipitate formed by adding a slight excess of silver nitrate to a measured volume of the acid.

[1] Treadwell-Hall, Analytical Chemistry, Vol. II, pp. 548 and 597 (1914).
[2] *Ibid.*, p. 548.

Tenth-normal Sodium Hydroxide.—Standardize this against the hydrochloric acid, using methyl orange as an indicator. In carrying out the standardization of any solution it is advisable to use at least 20 cc. so that the error of reading the burette will not affect the final result by more than one part in one thousand.

Methyl Orange.—Dissolve 0.02 g. in 100 cc. of water and filter the solution.

Barium Hydroxide.—The solution may be prepared as described on p. 150 and kept in a large bottle as shown in Fig. 114*a*.

Water Free from Carbonic Acid.—See p. 149.

Procedure.—Weigh out 1 g. of pig iron or 2 g. of steel and carry out the combustion as described in Method 3. If an

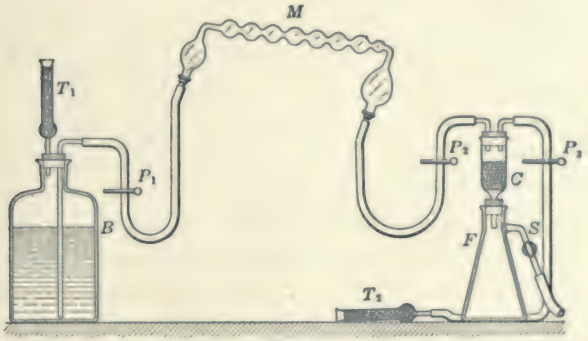

FIG. 117.

electric furnace is not available, a gas-heated furnace may be used. If it is not possible to maintain a temperature of at least 1000° with the latter, the combustion of the sample may be aided by placing the metal on a bed of ignited alumina (or alundum) and covering the sample with pure red lead. It is necessary to run a blank using the same quantity of the red lead.

When the combustion is complete, filter off the barium carbonate as described on p. 151, or, using Cain's directions, in the following manner:

Connect the absorption bulb as shown in Fig. 117. *S* is a two-way stopcock connected with suction. The bubble tube (Meyer tube) is fitted with two rubber stoppers through which short pieces

of glass tubing pass. The filter C contains a perforated porcelain plate at the bottom; it should slip easily up and down the funnel. Cover the porcelain plate with a felt of asbestos, which has been cleaned by heating several hours with strong hydrochloric acid and then by washing free from acid. Place on top of this a layer of similarly cleansed quartz to the height shown in the drawing. A mixture of grains such that about one half passes through a 20-mesh sieve and the remainder through a 10-mesh sieve is suitable. Instead of using the quartz alone, a mixture of quartz and asbestos works well. Fill the funnel with a suspension of asbestos and then wash the quartz into the funnel by means of a strong jet of water from the wash bottle, while maintaining gentle suction. In this way a filter may be prepared which is efficient and yet works rapidly.

Insert the stopper in the funnel and connect it with the Meyer tube as shown in the drawing and apply very gentle suction. When necessary open P_3 to admit air back of the liquid after the contents of the tube have all been transferred to the filter bottle, half fill the large bulb nearest B with water by opening the pinchcock P_1; operate the stopcock S during this and the subsequent operations so as to maintain gentle suction. Manipulate the tube M so as to bring the wash water in contact with all parts of the interior and then suck out the water through C; during this and the subsequent washings leave the pinchcock P_2 open. After eight washings, allowing the wash water to drain off thoroughly each time, detach M and complete the washing by filling C to the top with water free from carbonic acid, sucking dry and repeating the operation once more. Now admit air through the side opening of S, take away C, and transfer the contents of the filter funnel to an Erlenmeyer flask for the titration.

Add an excess of the standard acid from a burette and titrate the excess of alkali in the cold with standard sodium hydroxide, using methyl orange as an indicator.

After finishing the determination, rinse out the Meyer bulb carefully before using it again, to make sure that all the carbon dioxide is removed from it. Each day, before beginning work, it is well to rinse out the tube once with dilute acid and then several times with water. Also wash out the rubber tubing occasionally.

Computation.—One liter of normal acid, or alkali, is equivalent to 67.00 g. of pure sodium oxalate, 53.00 g. of pure sodium carbonate or 143.3 g. of silver chloride. If t cc. of hydrochloric acid solution were found in the standardization to be equivalent to a g. of sodium oxalate, sodium carbonate or silver chloride, according to the method of standardization, then

$$N_A = \frac{a}{t.e}$$

in which N_A represents the concentration of the acid in terms of a normal solution, e is 0.067 for sodium oxalate, 0.053 for sodium carbonate or 0.1433 for silver chloride, according to the method of standardization.

If, in titrating the acid against the base, it is found that r_1 cc. of acid are equivalent to r_2 cc. of the base, then the concentration of the sodium hydroxide in terms of a normal solution is shown by the expression

$$N_B = \frac{r_1}{r_2} N_A$$

One liter of normal acid, or alkali, is equivalent in this method to 6.00 g. of carbon, or 1 cc. = 0.00600 g. C. If, then, n_1 cc. of acid and n_2 cc. of base are used in the titration of the barium carbonate precipitate from s g. of material, we have

$$\text{Per cent. C} = \frac{\left(n_1 - n_2 \frac{r_1}{r_2}\right) 0.6 N_A}{s}$$

Test Analyses.—J. R. Cain and H. L. Cleaves tested this method against pure sugar, two samples of standardized Bessemer steel, and one sample of standardized pig iron. Using 0.0100 g. of sugar, the average error was + 0.00005 g. carbon, and the largest error in three experiments was + 0.00010 g. carbon. In three experiments with 0.0200 g. of pure sugar, the average error was + 0.00011 g. carbon and the largest error was + 0.00018 g. carbon. In three experiments with 0.0300 g. sugar, the average error was + 0.00015 g. carbon. The greatest error in these nine experiments with pure sugar corresponded to 0.9 per cent. of the total weight of sugar but as this represented a weight less than 0.0002 g. it is evident that the method is more

accurate than any method involving the weight of an absorption tube or bulb.

In eight experiments with iron and steel, using 1 g. samples in every case, the agreement was even better.

The method is less subject to disturbing influences and requires less elaborate apparatus than any of the methods which have been described. With a little practice, a precipitate can be filtered and prepared for titration within 5 min.

DETERMINATION OF GRAPHITE AND TEMPER CARBON

Principle.—Graphite and temper carbon are so similar in their chemical behavior that they cannot be separated by analytical methods. The precipitation and separation of combined carbon is based on the fact that graphite and temper carbon are not attacked by boiling dilute nitric acid, while the various forms of combined carbon form volatile compounds, or compounds soluble in nitric acid.

Procedure (Ledebur).—With dark gray cast iron use 1 g. with light gray or tempered iron 2 to 5 g., and with high nickel steel use 5–10 g. of the metal.[1] Weigh the sample into a 300–600 cc. beaker and heat it with dilute nitric acid (sp. gr. 1.2) using about 25 cc. of acid for each gram of metal. Immerse the beaker in cold water, or hold it under the tap, to prevent too violent action at the start with a consequent loss of material due to spattering. After the action has slackened, heat the beaker on a sand bath, or over an asbestos plate, until the metal is completely dissolved. If the sample contains much silicon (*e.g.*, gray pig iron) add ½ to 1 cc. of hydrofluoric acid[2] to dissolve the gelatinous silicic acid, which would otherwise clog the pores of the filter. Take care not to let any particles of paraffin from the acid container drop into the solution. Cover the beaker with a watch-glass and boil the solution very gently, over a small flame, for 1 or 2 hr. Then dilute with water,

[1] In determining graphite or temper carbon it is often better to use small pieces rather than turnings. This is especially true when it is a question of determining the amount of graphite or temper carbon in one place on a specimen. (See Part 1, p. 73.)

[2] It is best to pour the hydrofluoric acid into the beaker in such a way that it will not come into immediate contact with the glass.

set the beaker aside for a short time to allow the insoluble matter to settle, and filter through a well-fitting asbestos filter[1] into an Erlenmeyer flask.

After the liquid and residue have all been poured out of the beaker, rub the sides of the glass with a rubber-tipped stirring-rod to remove any adhering particles, then rinse the beaker with hot water and wash the filter and residue until free from acid.

The residue on the filter may be decomposed in a Corleis flask using the chrome-sulfuric acid method.[2]

For this purpose, remove the moist filter and residue from the funnel with a pair of pincers and spread it on a watch-glass. Wipe out the funnel with some ignited asbestos and add this to the major part. Throw all of the asbestos into the Corleis flask and oxidize the graphite or temper carbon exactly as described on p. 128.

The calculation is made in the same way as with total carbon.

Test Analyses.—The results of some graphite determinations are given in Table 82.

The determination of total carbon in the same samples gave the following values:

Sample 1 = 4.27 per cent.
Sample 2 = 0.76 per cent.
Sample 3 = 0.19 per cent.

[1] Asbestos for this purpose is prepared as follows: Cut long-fibered asbestos into pieces about 1 cm. long and heat them with successive portions of strong hydrochloric acid, until a portion of fresh acid is not colored appreciably yellow. Wash the asbestos free from acid with hot water, dry the mat of asbestos in the hot closet and finally ignite it in a porcelain crucible to destroy any organic matter.

To make the filter, place some of the ignited asbestos in the stem of an ordinary short funnel. By a stream from the wash bottle, distribute the fibers in such a way that the fine material will close the pores made by the coarser fibers and form a tight mat.

The filter is known to be tight if the funnel stem will stay full of water. An asbestos filter made in this way will filter rapidly and if enough asbestos is used will be tight enough to hold all but the most finely divided precipitates. Another method of preparing ignited asbestos is given on page 158.

[2] The combustion of graphite may also be carried out in a current of oxygen. To do this, transfer the asbestos containing the filtered carbon to a porcelain boat while still moist, dry it at 105° to 110° and burn it as described on p. 145, or on p. 159. Method 5, p. 161, may also be used.

TABLE 82

No.	Material	Exp.	Weight, sample	Gain in weight		Graphite, per cent.
				Tube 1	Tube 2	
1	Pig iron	*a*	1.0000	0.1260	[0]	3.44
		b	1.0000	0.1284	[0]	3.50
2	Nickel steel (24 per cent. Ni)	*a*	5.000	0.0156	[0]	0.58
		b	5.000	0.1056	[0.0024]	0.58
3	Nickel steel (26 per cent. Ni)	*a*	6.00	0.0054	[0.0006]	0.02
		b	6.00	0.0052	[0.0008]	0.02

CHAPTER II

SILICON

1. DETERMINATION IN MATERIALS SOLUBLE IN ACID

Principle.—On treating iron and steel with acid, the silicon present as silicide is changed to hydrated silicon dioxide, commonly called silica. It is probable that during the treatment with acid there is an intermediate formation of volatile, easily decomposable substances such as SiH_4 and $SiCl_4$. Thus when iron silicide reacts with hydrochloric acid, the reaction

$$FeSi + 6HCl = FeCl_2 + SiCl_4 + 3H_2$$

may take place, but the silicon chloride, as fast as it is formed, reacts with the water present to form hydrated silicon dioxide:

$$SiCl_4 + 2H_2O = SiO_2 + 4HCl$$

This second stage of the reaction takes place so quickly that there is never any loss of silicon by volatilization (*cf.* Test Analyses, pp. 176, 180). The silicon dioxide, to a considerable extent, remains dissolved as colloid (*sole*). By evaporating the hydrochloric (or sulfuric) acid solution and heating the residue to at least 135° the colloidal silicic acid becomes dehydrated sufficiently to convert the colloid into the insoluble form (*gele*) and by washing with hydrochloric acid it can be freed from the soluble chlorides of the other metals.

Method A. Solution of the Sample in Hydrochloric Acid

Procedure.—Weigh out 2 to 4 g. of gray cast iron or silicon steel (up to 5 per cent. Si), or 5 to 10 g. of white cast iron, ingot iron, wrought iron or ordinary steel, into a porcelain casserole of 12 to 15 cm. diameter. Cover the casserole with a watch-glass and dissolve the metal in hydrochloric acid, sp. gr. 1.12, using 10 cc. of acid for each gram of metal.

When the main reaction is over, place the casserole on the water bath and heat till the solution of the material is complete. Then rinse off the bottom of the watch-glass, to remove any silicon dioxide that may have spattered upon it, and evaporate to dryness. Place the dish containing the dry residue upon a Finkener tower (Fig. 118) and heat for about an hour, until no more fumes of hydrochloric acid are evolved and the contents of the dish have become brown. During this heating, the dish should be frequently turned to secure uniform heating of the residue. Instead of using the Finkener tower, the casserole and its contents may be heated for an hour in a hot closet kept at about 135° or upon a sand bath.

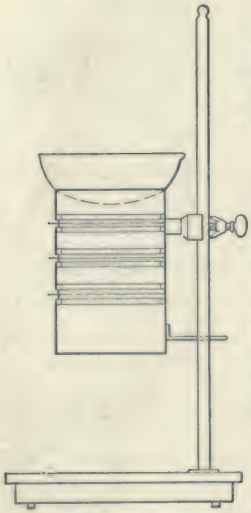

FIG. 118.

After the above heating, cover the dish with a watch-glass and allow it to cool. Without removing the watch-glass, cover the cool residue with hydrochloric acid (sp. gr. 1.12), using about 10 cc. for each gram of original substance, and heat upon the water bath until the chlorides are entirely dissolved, from time to time stirring the liquid with a glass rod.

If a dark-brown residue of ferric oxide or basic salt remains undissolved at the bottom of the dish, it is because the residue was heated too strongly. In such cases, evaporate the solution again to dryness and, without further heating, take up the residue in concentrated hydrochloric acid (sp. gr. 1.2).

Dilute the solution with about 150 cc. of water, heat nearly to boiling, and filter promptly[1] through a 9 cm. filter.[2]

If the original material contained considerable silicon and there is danger of the filter becoming clogged or of the filtrate running through turbid, it is well to add some filter-paper pulp

[1] If the solution stands long before filtering a little silica dissolves.

[2] In all cases where the precipitate is to be weighed, a filter washed with sulfuric and hydrofluoric acids must be used; the ash of such a filter weighs less than 0.1 mg.

before filtering. The pulp is prepared by shaking small pieces of filter paper with hot water in a stoppered Erlenmeyer flask.[1]

After all the liquid has passed through the filter, transfer as much as possible of the precipitate to the filter by means of a stream of water from the wash bottle, and remove the last traces of precipitate from the sides of the dish by rubbing with a piece of filter paper which has been moistened with alcohol. The paper may be rubbed directly with the finger or with the aid of a glass rod covered on the end with smooth rubber tubing (a "policeman").[2]

Wash the filter and residue with hot, dilute hydrochloric acid (1 :5) until the filtrate gives no blue color with potassium ferricyanide solution. While still moist, place the filter and precipitate in a weighed platinum crucible, place the latter on its side in a triangle and dry carefully by a small flame placed near

[1] The rate at which the solution runs through the filter is influenced largely by the way the paper is folded (*cf.* Raaschou, Z. anal. Chem., **49**, 759 (1910). Filters which lie against the funnel all along the sides often work badly, whereas filters which adhere to the sides of the funnel only near the top, with the rest of the paper hanging free, permit the more rapid passage of the solution through them. For this reason, it is well to make the second fold of the filter a little wider than a right angle. To prevent the formation of a channel through which a part of the precipitate may be sucked, it is well to tear off a little of the inside edge as shown in Fig. 119.

Fig. 119.

To place the paper in the funnel, take hold of the funnel with the left hand, insert the folded filter and hold it firmly in position with the index finger of the left hand. Then fill the filter with water by a stream from the wash bottle, stopper the funnel tube with the finger, raise the filter a little to allow the air in the funnel tube to escape, replace the filter in its proper position and press out the air bubbles between the paper and the glass sides of the funnel. Then allow the water to run through the funnel and pour more water upon the filter.

In filtering, keep liquid in the funnel but do not allow the level to rise higher than the top of the paper.

Under no circumstances should a filter be used that is large enough to completely fill the funnel. The use of a filter extending above the funnel is never permissible in quantitative work.

[2] When a little tungsten is present, a yellow film usually adheres very firmly to the sides of the procelain dish. This may be removed by rubbing with filter paper moistened with ammonia. (*cf.* Tungsten, p. 324.)

the mouth of the crucible. When all the moisture has been expelled, transfer the flame to the base of the crucible and destroy the paper at as low temperature as possible without allowing it to take fire. Finally ignite strongly, using the blast lamp if the quantity of silica is considerable. Cool in a desiccator[1] and weigh. Repeat the ignition and weighing until a constant weight is obtained.

In the analysis of white cast iron, wrought iron, steel, etc., the precipitate of silicon dioxide usually appears gray colored on the filter but is perfectly white after being ignited. In no case, however, where accurate results are desired, should it be regarded as perfectly pure but its purity must be determined by treatment with sulfuric and hydrofluoric acids, whereby volatile silicon fluoride is formed.

To this end, moisten the silicon dioxide in the platinum crucible with sulfuric acid[2] (1:1), add from 1 to 3 cc. of pure hydrofluoric acid,[3] and evaporate as far as possible on the water bath. Place the crucible on the Finkener tower[4] and gradually raise the temperature until all the free sulfuric acid has been expelled, then decompose any sulfates by direct ignition over the free

[1] *cf.* p. 194, footnote.

[2] The addition of the sulfuric acid has a double purpose. On the one hand, it aids the reaction between silica and hydrofluoric acid by acting as a dehydrating agent and prevents the formation of fluosilicic acid by the interaction of silicon fluoride and water. On the other hand, it prevents the volatilization of other fluorides, such as those of aluminium, iron, chromium, titanium and vanadium. When these last-mentioned elements are present, they will be volatilized to some extent as fluorides if too little sulfuric acid is used, and the silicon result will be too high. Sulfuric acid decomposes these fluorides before their boiling points are reached and the sulfates are decomposed upon further heating into oxide and sulfuric anhydride, thus leaving them in the same condition as before the treatment. The amount of sulfuric acid to be added should be regulated by the probable amounts of these impurities. When tungstic acid is present, the ignition before and after treatment with hydrofluoric acid must *not* be over the blast lamp. Tungstic acid is slightly volatile when heated with sulfuric acid in a platinum crucible.

[3] The purity of the acid should be tested by evaporating some of it to dryness and making sure that there is no weighable residue after ignition.

[4] Instead of using the water bath and Finkener tower, the evaporation of the acid may take place by suspending the crucible in a larger iron crucible (by inserting platinum wires in the latter) and heating over the free flame.

flame, using a high temperature at the last, cool in a desiccator, and weigh. The loss on volatilization represents the weight of pure SiO_2:

$$SiO_2 + 4HF = SiF_4 + H_2O$$

Usually, in spite of all the pains that may be taken with the analysis, small quantities of ferric and manganic oxides remain behind after the treatment with hydrofluoric acid, and in the analysis of steels containing tungsten, titanium, chromium, and vanadium these elements are invariably present in the residue to a greater or less extent.

In the determination of silicon in gray cast iron, all the graphite remains behind with the silica and care should be taken to burn it completely before weighing. It is almost impossible to obtain a silica precipitate so pure that the treatment with hydrofluoric acid is unnecessary but a more complete removal of the iron may be accomplished if, after washing with dilute hydrochloric acid on the filter, the silica is washed well with alcohol to remove substances formed by the decomposition of carbide, and again with hydrochloric acid to the disappearance of the iron test.

Small quantities of silicic acid remain in the first filtrate but when the work is done carefully according to the above directions the silica thus lost will rarely amount to more than a fraction of a milligram and this is more than balanced by the amount of silica that is obtained from the reagents and from the dishes. In iron and steel analysis, therefore, it is unnecessary to evaporate the filtrate from the silica precipitate to recover more silica, although this is usually necessary in the analysis of silicates.

The filtrate from the silica determination, together with any residue from the treatment with hydrofluoric acid, may be used for the determination of manganese, copper, nickel, chromium, aluminium, etc., but not for the determination of phosphorus or sulfur.

Method B. Solution of the Sample in Nitric Acid

Weigh out the same amount of metal as stated for Method *A* and add 12 cc. of nitric acid (sp. gr. 1.18) for each gram of metal. Add the acid in small portions, waiting each time till the violent

reaction is over. When all the acid has been added, heat on a water bath until the sample has all dissolved. If there is turbidity due to a brown deposit, bring this into solution by adding more nitric acid and heating until eventually a fairly clear, more or less dark brown colored solution is obtained. Remove the watch-glass and evaporate on the water bath as near dryness as possible. Since a film forms on the surface of the liquid which makes it difficult to evaporate to dryness, rotate the solution about the dish from time to time so that liquid collects on top of the dry layer.

It is not advisable to hasten the evaporation by constantly stirring with a glass rod because, during the subsequent heating, pieces of the glass are likely to splinter off the rod and render the determination of the silicon inaccurate.

To remove all the nitric acid, heat the dish upon the Finkener tower or on a sand bath. Another way is to heat the dish on a piece of asbestos plate, 3 mm. thick, over a Fletcher burner, taking care to heat gently at first.

Care must be taken to avoid loss by spattering. When no more bubbles of gas are evolved, remove the cover glass and heat the contents of the dish still hotter until the nitrates are decomposed (in using the Finkener tower, remove the wire gauze). Finally, cover the dish with a watch-glass and ignite over a free flame until no more red vapors are evolved, showing that the decomposition of the nitrates is complete. The oxides are now dark brown and do not adhere very firmly to the sides of the casserole.

Allow to cool, moisten with a little concentrated hydrochloric acid (sp. gr. 1.19) and warm for a short time. Then add 10 cc. of hydrochloric acid (sp. gr. 1.12) for each gram of metal and heat, while stirring with a glass rod, until all the ferric oxide dissolves.

To make sure that the silicon dioxide is all in the insoluble condition, evaporate the hydrochloric acid solution to dryness and heat for some time at 135°. After cooling, moisten the residue with concentrated hydrochloric acid (sp. gr. 1.19) and then add the same volume of hydrochloric acid (sp. gr. 1.12) as before, dilute, filter and wash with dilute hydrochloric acid until

the washings give no test for iron with potassium thiocyanate solution.

With material free from graphite, the silicon dioxide is obtained by this method in the form of a white or nearly colorless gelatinous precipitate; if tungsten is present it is indicated by its yellow color.

With materials containing graphite, the precipitate requires the same treatment as is recommended under Method *A*. In all cases the treatment with hydrofluoric acid is necessary.

The filtrate from the silica can be used for the determination of substances such as manganese, copper, nickel, aluminium, chromium, phosphorus and iron, but not for the determination of sulfur.

Method C. Solution in Nitric Acid and Addition of Sulfuric Acid

In this method, which was proposed by T. M. Drown[1] and is regarded as a standard method in the United States, the sample is dissolved as in Method *B*, sulfuric acid is added and the solution is evaporated until copious fumes of sulfuric anhydride are evolved. The hot, concentrated sulfuric acid acts as a very efficient dehydrating agent, thus making the silicon dioxide insoluble. The method is much more rapid than either of the above and the results are equally accurate.

Procedure.—Dissolve 1 g. of cast iron in 20 cc. of nitric acid (sp. gr. 1.2) in a platinum or porcelain dish. When all action has ceased, add 20 cc. of sulfuric acid (1 : 1) and evaporate until dense fumes of sulfuric anhydride are evolved. During the final heating the dish should not be covered with a watch-glass because the water that condenses in the glass will cause spattering as it drops into the hot sulfuric acid. Allow to cool, dilute with 150 cc. of water and heat carefully until all the ferric sulfate is dissolved. Filter the hot solution and wash first with hydrochloric acid (sp. gr. 1.1) and then with hot water. The further treatment of the precipitate is the same as in the other methods.

[1] J. Inst. Min. Eng., **7**, 346.

Computation.—If p = wt. of SiO_2, s = wt. of substance, then

$$\text{Per cent. Si} = \frac{\text{Si} \times p \times 100}{\text{SiO}_2 \times s} = \frac{46.93\,p}{s}$$

The computation is the same for all three of the methods.

Test Analyses.—Experiments with steel containing 0.33 per cent. Si, silicon steel with 1.65 per cent. Si, chrome steel with 0.20 per cent. Si and chrome-tungsten steel with 0.23 per cent. Si have shown that practically identical values are obtained with Methods *A* and *B* and the results by various chemists on standard steels and cast irons prepared by the Bureau of Standards at Washington, D. C., show that Method *C* is capable of giving equally exact results. A high vanadium content of the steel does no harm.

Accuracy of the Results.—The chief sources of error in the determination of silicon are:

1. Silicic acid present in the acids.
2. Solution of silica from the porcelain dish.
3. Solubility of silicon dioxide in hydrochloric acid solutions containing ferric chloride.
4. Presence of non-volatile material (oxides of iron, aluminium or of the alkalies) in the hydrofluoric acid.

The first two sources of error tend to cause the results to come out too high and the last two sources tend to give too low results. The errors, therefore, may compensate one another.

The extent of error arising from the first and second sources should be determined by blank tests carried out with the same amount of acid as in the analysis. The quantity of silica thus found should be deducted from that obtained in the analysis. The silicic acid content of acids increases slowly up to a certain point upon standing in glass bottles. The silica obtained by evaporation in porcelain dishes is usually a very small quantity.

The hydrofluoric acid should be tested to see if the quantity used in the analysis leaves a weighable residue. This is not usually the case with the best grades of hydrofluoric acid.

As regards the solubility of silicon dioxide in hydrochloric acid solutions containing iron, there are very few statements in the literature. It is pretty certain, however, that this error is not large and probably does not exceed the error in weighing. There

is always a tendency for the deposited gelatinous silicic acid to pass into the colloidal condition and this tendency becomes noticeable if the solution is allowed to stand some time before filtering.

It is probably safe to assume, however, that the error in a silicon determination when carefully carried out is not greater than ± 1 mg. and on a 1 g. sample this would amount to 0.05 per cent. or on a 10 g. sample to 0.005 per cent. It follows, therefore, that the results should not be regarded as accurate beyond the second decimal and a silicon content below 0.01 per cent. cannot be determined with accuracy by any one of the above methods.

Permissible Deviation of Silicon Values.—Corresponding to the sources of error and the accuracy attainable in the determination, the following table represents the allowable deviation in duplicate results on the same sample.

Si content	Allowable error
0.01 to 0.25 per cent.	0.005 per cent.
0.25 to 1.00 per cent.	0.01 per cent.
1.00 to 5.00 per cent.	0.02 per cent.
5.00 to 10.00 per cent.	0.03 per cent.

Applicability of Methods A, B, and C.—All grades of iron and steel that are soluble in hydrochloric acid or nitric acid and most other metals or alloys that are soluble in these acids (*e.g.*, nickel, chromium, manganese, aluminium, zinc, molybdenum) may be analyzed for silicon by any of the above methods.

Irons containing up to 5 per cent. silicon can be dissolved without much difficulty but incomplete solution always results when the silicon content is much higher; in such cases, therefore, these methods have no advantages over the fusion methods described under **2.**

2. DETERMINATION OF SILICON IN MATERIALS INSOLUBLE IN ACID

Principle.—Finely pulverized metals and alloys can be attacked by heating with a mixture of pure sodium carbonate and pure magnesium oxide.

The chemical reaction that takes place is,[1] in the first place, an oxidation, and depends upon the tendency of sodium carbonate to decompose into sodium oxide and carbon dioxide; the latter acts upon the metals forming metal oxide and carbon monoxide.[2] Similarly, the reaction that takes place with the metalloid silicon may be expressed as follows:

$$(a)\ Na_2CO_3 \rightleftarrows Na_2O + CO_2$$
$$(b)\ Si + 2CO_2 = SiO_2 + 2CO$$
$$(c)\ SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$

The addition of magnesium oxide prevents the mass from fusing and as a result the carbon dioxide passes off more readily and without the danger of loss by spattering that would result if the flux were liquid.

After ignition, the mass is dissolved in water and dilute acid and the silica is determined as already described.

Ignition Mixtures.—It is well to have two mixtures at hand, one consisting of two parts sodium carbonate to one part magnesium oxide, the other of one part sodium carbonate and two parts magnesium oxide. The mixtures should be thoroughly incorporated by rubbing in a mortar. The first mixture was proposed by Rothe[3] and the second by Eschka.[4] As a rule the Rothe mixture is used but, when fusion results with it, the Eschka mixture is required.

Procedure.—The chief requirement for the success of the ignition process is that the material shall be in the form of very fine powder. The finer the powder, the more rapid and the more complete the attack. Coarse pieces may be broken up in a diamond mortar and then, if possible, ground in an agate mortar until all the powder passes through a 120-mesh sieve.

Of material rich in silicon (metallic silicon, ferro-silicon) take from 0.3 to 1 g., but of alloys with low silicon content (ferro-

[1] Sodium carbonate alone may be used in some cases but the metal is attacked less readily and there is more danger of loss by spattering.

[2] Deiss, Chem.-Ztg., **34**, 781 (1910).

[3] Mitt. kgl. Materialprüfungsamt, **25**, 51 (1907).

[4] Z. anal. chem., **13**, 344 (1874).

chrome, ferro-tungsten, etc.) take up to 5 g. For the ignition, a spacious platinum crucible is required and it should be thoroughly cleaned by fusing sodium carbonate in it and washing with water and dilute acid. Before introducing the sample, cover the bottom of the clean crucible with a layer 3 to 4 mm. deep of the sodium carbonate and magnesia mixture. Mix the weighed sample in a clean agate mortar with 7 to 8 times as much of the ignition mixture and then transfer the powder without loss to the crucible (using glazed paper beneath the crucible to catch any powder that is spilt). Clean the mortar and pestle by rubbing with a little more of the ignition mixture, and add the latter to the contents of the crucible. Then place the cover on the crucible and heat strongly for half an hour using a good burner, and finally heat 30 min. to 1 hr. over the blast lamp. Or, if an electric muffle furnace is at hand, it may be used to advantage. In this case the crucible should not come into direct contact with the glowing walls of the muffle as there is danger of both crucible and muffle being injured; the crucible should be placed upon a platinum triangle, with the three ends of the latter bent vertically downward and resting on the bottom of the muffle (*cf.* Fig. 128).

When the ignition is accomplished, remove the crucible and allow it to cool. The cake within the crucible should be sintered into a coherent mass without being at any place fused to the sides of the crucible. By simply inverting the crucible the cake should fall out, leaving the crucible nearly clean. The crucible is not attacked appreciably and experiments have shown that after igniting several grams of different alloys there is no sensible loss in weight of the crucible.

Soften the mass in a porcelain casserole by treatment with water; wash out the crucible well and dissolve any adhering solid by heating with dilute hydrochloric acid, adding the solution to the contents of the porcelain dish. Cover the dish with a watch-glass, add hydrochloric acid until the sodium carbonate is all decomposed and heat on the water bath until all the magnesia, iron oxide, etc., is dissolved. For 10 g. of the ignition mixture, about 45 cc. of hydrochloric acid (sp. gr. 1.12) are required. Evaporate the solution on the bath as far as possible and complete the necessary dehydration of the silicic acid by the

customary heating to 135°.[1] After cooling, moisten with concentrated hydrochloric acid (sp. gr. 1.19), add the usual quantity of hydrochloric acid (sp. gr. 1.12) and heat until all the soluble salts have dissolved.

Dilute the solution with water, filter off the silica, wash with dilute hydrochloric acid and test the filtrate for silica by evaporating again to dryness, repeating the treatment of the residue as above, and filtering through a fresh filter.

If the precipitated silicon dioxide should be contaminated with heavy dark particles of unattacked material (distinguishable from any graphitic particles by the gritty feeling under a stirring rod) then the precipitate, after being washed well, must be ignited and fused with sodium carbonate in a platinum crucible. From this fusion, the silica is recovered in the same manner as described above for the treatment of the mass after the original ignition.

After igniting the silica to constant weight, determine its purity by treatment with sulfuric and hydrofluoric acids.

Test Analyses.—By this method, duplicate determinations agreed within 0.1 per cent. in the analysis of samples of ferrosilicon containing respectively 78 per cent. and 92 per cent. Si and of silico-manganese having 23 per cent. Si.

Accuracy of the Results by the Ignition Method.—Inasmuch as the weights of sample taken for analysis by this method are not usually as large as those taken for analysis by the other methods, it is evident that an error of 1 mg. in the weight of silicon dioxide will have a greater effect upon the percentage of silicon found. For this reason the accuracy of the results by this method is less.

Errors may be introduced by a silica content of the flux. To avoid this error, a blank determination should be carried out with the same quantity of flux that is used in the analysis and the quantity of silica found should be deducted from that found in the actual determination. It is possible, however, to buy sodium

[1] On account of the presence of magnesium chloride, the evaporation to dryness requires more time than usual and in the subsequent heating of the moist residue special care must be taken to avoid loss by spattering. The residue must not be heated above 135° as the magnesium chloride forms a basic salt which combines to some extent with silica if heated too much.

carbonate and magnesium oxide so pure that the silica from 10 g. of the Rothe mixture is not weighable.

Permissible Deviations in the Silicon Values by the Ignition Method.—Taking into account the various sources of error as far as they concern the determination of silicon in materials rich in this element, the permissible deviation in duplicate determinations may be placed as follows:

Silicon content	Allowable error
1 to 10 per cent.	± 0.05 per cent.
10 to 20 per cent.	± 0.10 per cent.
20 to 50 per cent.	± 0.15 per cent.
50 to 100 per cent.	± 0.2 per cent.

Applicability of the Ignition Method.—The method is suitable for the determination of silicon in metals and alloys which are insoluble or difficultly soluble in acids, provided it is possible to get them in finely powdered form. The method has to be modified for the analysis of titanium alloys, inasmuch as solutions containing titanium are likely to yield silica precipitates containing a large part of the titanium in the form of hydrated titanium dioxide.

Modification of the Silicon Determination for Titanium Alloys.—Decompose the titanium-silicon alloy with the Rothe or Eschka mixture in the usual manner and soften the ignited mass with cold water; triturate the sintered lumps in an agate mortar and rinse everything into a beaker. Carefully avoiding any heating of the solution, add hydrochloric acid (sp. gr. 1.12) until the liquid is strongly acid. Allow the contents of the beaker to stand for an hour or two in the cold. Then heat slowly on the water bath, with frequent stirring, until a clear solution is obtained in the course of a few hours. Add 20 cc. of sulfuric acid (1:1) and evaporate until all the hydrochloric acid is expelled. Transfer the contents of the beaker to a platinum dish and heat on the Finkener tower until white fumes of sulfuric anhydride are evolved. As soon as this is accomplished, stop heating and allow the dish to cool. Add water to the residue, filter off the silica and wash it free from iron with dilute hydrochloric acid. Ignite, weigh and treat with sulfuric and hydrofluoric acids as usual.

Test Analyses.—In the analysis of metallic titanium, duplicate determinations on 1 g. samples gave 4.79 per cent. and 4.69 per cent. Si. In the analysis of ferro-titanium, 0.85 and 0.51 g. of material were taken for analysis and the results obtained were 3.65 per cent. and 3.60 per cent. Si.

CHAPTER III

MANGANESE

The manganese content of iron and steel varies considerably. In ingot iron it is usually very low and in ordinary steel it rarely amounts to more than 1 per cent. In manganese steel and in certain other special steels, however, much more manganese is present. Certain grades of cast iron contain considerable manganese and in ferro-manganese, silico-manganese, chrome-manganese, and other manganese alloys, this element constitutes the most important constituent.

1. GRAVIMETRIC DETERMINATION OF MANGANESE

Principle.—One of the best methods for separating manganese from iron in the analysis of cast iron, steel and other alloys low in manganese, is the Rothe ether separation which is based upon the fact that ferric chloride is very soluble in ether whereas manganese chloride is not.

If two non-miscible solvents are in contact with one another and a third substance is present which is soluble in both liquids, the ratio of the concentrations (quantities present in a unit of volume of each solvent) of this substance in the two solvents after equilibrium has been established will be constant at any given temperature provided the solute has the same molecular weight in both solutions. This is the so-called *distribution law*. The ratio $\frac{c_1}{c_2} = k$, where c_1 represents the concentration in one solution and c_2 the concentration in the other, is called the *distribution coefficient.*

After removing the ferric chloride by shaking the hydrochloric acid solution with ether, it is then a question of separating the manganese from other metals and acids that are not dissolved by the ether but remain in the hydrochloric acid solution.

Test Analyses.—In the analysis of metallic titanium, duplicate determinations on 1 g. samples gave 4.79 per cent. and 4.69 per cent. Si. In the analysis of ferro-titanium, 0.85 and 0.51 g. of material were taken for analysis and the results obtained were 3.65 per cent. and 3.60 per cent. Si.

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If two non-miscible solvents are in contact with one another and a third substance is present which is soluble in both liquids, the ratio of the concentrations (quantities present in a unit of volume of each solvent) of this substance in the two solvents after equilibrium has been established will be constant at any given temperature provided the solute has the same molecular weight in both solutions. This is the so-called *distribution law.* The ratio $\frac{c_1}{c_2} = k$, where c_1 represents the concentration in one solution and c_2 the concentration in the other, is called the *distribution coefficient.*

After removing the ferric chloride by shaking the hydrochloric acid solution with ether, it is then a question of separating the manganese from other metals and acids that are not dissolved by the ether but remain in the hydrochloric acid solution.

necessary to add ether-hydrochloric acid solution *A* until 6 cc. of the latter are present for each gram of dissolved iron. Shake the solution and cool. This addition of the ether-hydrochloric acid serves partly to give the proper hydrochloric acid concentration for a succesful separation by ether and it also serves to prevent, as far as possible, the evolution of heat which takes place when ether is added to a hydrochloric acid solution of ferric chloride.

Next, add ether until the upper bulb is nearly full, close the stopcock and shake. If the upper bulb becomes at all warm, cool under running water.

Fasten the shaking funnel, at the narrow part above the upper bulb, in a clamp attached to a ring stand and allow the liquid to remain quiet for some time. In this way, two layers are obtained. The upper layer is green and consists chiefly of ferric chloride dissolved in ether. The lower layer consists of a hydrochloric acid solution containing the chlorides of most of the other constituents of the material which is being analyzed. Some hydrochloric acid is present in the ether solution and some ether is present in the lower layer. The color of the latter varies according to what metals other than iron are present in the original substance.

When chromium, nickel or much vanadium is present, the color of the hydrochloric acid solution is green or bluish-green; if these elements are absent the solution is usually yellow owing to the presence of small quantities of ferric chloride. Often, a brownish-yellow solution is obtained when titanium is present; with considerable titanium and insufficient acid it sometimes happens that flakes of titanium dioxide are deposited (*cf.* p. 309).

By opening both the upper and middle stopcocks, allow the hydrochloric acid solution to run into the lower bulb but take care to close the middle stopcock as soon as the line of demarcation between the two layers of liquid is reached; none of the upper ethereal solution should pass into the middle lower bulb at this time, or into the boring of the middle stopcock. Allow the solution in the upper bulb to stand a little longer and again drain off the hydrochloric acid. To wash out the boring of the middle stopcock, add a few cubic centimeters of ether-hydrochloric acid solution *B*, and, without shaking, drain off the acid

that collects below the ether into the lower bulb. The upper bulb now contains an olive green solution chiefly of ferric chloride and hydrochloric acid in ether, and the lower bulb contains an aqueous hydrochloric acid solution of the chlorides of manganese, nickel, cobalt, etc. To remove small quantities of these last elements that remain adhering to the ether solution in the upper bulb, add 10 cc. of ether-hydrochloric acid solution *B*, and to remove small quantities of ferric chloride that are present in the solution contained in the lower bulb, nearly fill it with ether. Close both stopcocks and shake well. After the layers have formed again, the lower layer in the upper bulb contains some more of the manganese, etc., together with a little ferric chloride that has been shaken out of the ether. In the lower bulb, however, the bottom layer ought not to contain more than 1 or 2 mg. of iron. It is the purpose of subsequent treatment to remove all the metal chlorides except ferric chloride from the ether layer in the upper bulb and to free these hydrochloric acid extracts from iron as far as possible by shaking in the lower bulb with ether containing very little ferric chloride.

Allow the hydrochloric acid solution in the lower bulb to run into the porcelain dish that was used previously in the analysis, and rinse out the boring of the stopcock and the tubing below it with a few cubic centimeters of ether-hydrochloric acid solution *B*. Then allow the lower layer in the upper bulb to flow into the lower bulb and likewise rinse the upper bulb with a little ether-hydrochloric acid. To remove more of the metal chlorides from the ether in the upper bulb, again add 10 cc. of ether-hydrochloric acid solution *B*, shake and remove the bottom layers in each bulb by the same operations as before. After the two layers have separated in each bulb, add the lower layer in the bottom bulb to the contents of the porcelain dish and allow the lower layer in the upper bulb to drain into the lower bulb. To be on the safe side, repeat this treatment with 10 cc. of ether-hydrochloric acid solution *B* a third and fourth time. Then, as a rule, the separation is as complete as is necessary and it may be assumed that the solution in the porcelain dish now contains all the manganese, nickel, cobalt, chromium, aluminium, copper, titanium, sulfuric acid, phosphoric acid, and vanadium together with small quantities of iron.

Large amounts of alkali salts cause trouble; the ether causes them to precipitate and the deposited salts tend to clog the borings in the stopcocks. For this reason the use of alkali salts must be avoided in preparing a solution for treatment with ether. Thus oxidation must be accomplished with nitric acid rather than with potassium chlorate and any excess of acid removed by volatilization rather than by neutralization with ammonia.

In the apparatus, the iron is left as ferric chloride dissolved in ether and hydrochloric acid. By shaking with water, the greater part of the ether can be separated from the ferric chloride and the solution of the latter may be used for the determination of iron (*cf.* p. 319). When the method is used frequently, it is well to recover the ether. After washing it with sodium hydroxide solution, and drying over calcium chloride, it can be easily distilled from a steam bath. It is necessary to keep all gas flames away from the vicinity of the distilling apparatus on account of the danger of the vapors taking fire.

FIG. 121.

Drive off the ether from the hydrochloric acid extract containing the manganese and other metals by heating the porcelain dish at one of the cooler places on the steam bath and then evaporate to dryness. Take up the residue in a little dilute hydrochloric acid, rinse the solution into a 100-cc. beaker and precipitate any copper present by the addition of a few cubic centimeters of saturated hydrogen sulfide water, stirring with a glass rod until the copper sulfide precipitate collects together and settles. Then filter into the original porcelain dish, add a little sulfuric acid to the filtrate and evaporate to dryness. Dissolve the residue in a little dilute sulfuric acid and transfer the solution to a platinum dish of 11 to 13 cm. diameter (Fig. 121). The quantity of sulfuric acid used must be adjusted so

that in the following evaporation all the chlorides present will be changed to sulfates and upon stronger ignition (on the Finkener tower) a slight excess will be evolved in fumes. After this treatment is accomplished, allow the dish to cool. It is now ready for the fusion.

Fusion with caustic soda serves to free the manganese (together with any nickel, cobalt and iron), from phosphoric acid, chromium, vanadium and aluminium.

According to the amount of sulfates present, dissolve from 2 to 5 g. of pure sodium hydroxide in a platinum crucible with as little water as possible, and add the solution to the contents of the platinum dish. The metal salts are at once decomposed by the alkali. Take hold of the dish in some such way as shown in Fig. 121, and carefully evaporate the solution to dryness by moving the dish back and forth over a small Bunsen flame. Too rapid evaporation will cause loss by spattering. Continue the heating till the solid melts but avoid overheating. When a quiet fusion is obtained, allow the mass to cool somewhat and sprinkle over the top a little potassium chlorate or sodium peroxide (a quantity such as can be held on the point of a penknife suffices). Turn up the Bunsen flame just a little and heat the dish, while moving it about, until the entire contents are fused and no lumps of undecomposed sodium peroxide are visible.

Heating any part of the dish more strongly than is necessary to accomplish fusion must be avoided, as otherwise the platinum dish will be attacked. If care is exercised, however, this operation can be carried out with either potassium chlorate or sodium peroxide without the platinum dish being injured.

After cooling the fusion, remove the holders, cover the dish with a watch-glass and dissolve the contents by adding about 60 cc. of hot water; any excess of sodium peroxide is decomposed by this treatment and oxygen is evolved. Treat the solution, which is usually colored green by manganate, with a little more sodium peroxide; this decomposes the manganate, forming manganese dioxide with evolution of oxygen.

To destroy the excess of sodium peroxide, heat the covered dish and its contents for half an hour on the steam bath. Then rinse into a 300 to 400 cc. beaker, dilute with water to about 200 cc. and allow the precipitate to settle. Usually a slight yellowish-

brown stain remains in the platinum dish. Dissolve this with a little dilute sulfuric acid and a small crystal of oxalic acid but do not add this solution to the main solution at present.

In the analysis of most iron and steel samples, the solution above the manganese dioxide precipitate (which also contains nickel, cobalt and iron) is usually colored more or less yellow by a little chromium. Allow the solution to cool, and, without stirring up the precipitate, decant the clear, supernatant liquid through 7 or 9 cm. filter, according to the size of the precipitate. Add hot water to the precipitate, allow it to settle and again decant. Repeat this operation once or twice more, and place a fresh beaker, or Erlenmeyer flask, under the funnel. Then, if subsequent washings run through the filter turbid, it will not be necessary to refilter the entire solution. Transfer the precipitate to the filter and wash it carefully. When the alkali salts are all removed there is danger of some of the precipitate becoming colloidal and passing through the filter. This may be avoided, if toward the end of the washing a dilute solution of ammonium sulfate is used instead of pure water, or if from time to time a small crystal of ammonium sulfate is placed in the filter and the washing done with pure water.

The combined filtrate contains all the chromium and aluminium besides the phosphorus and vanadium. It can be used for the determination of these elements.

Upon the filter are the hydrated oxides of manganese, nickel and cobalt together with a little iron that remained in the aqueous solution after treatment with ether. Dissolve the precipitate in a little concentrated hydrochloric acid. If there is much precipitate, wash as much as possible into a small beaker, place the beaker under the funnel and dissolve the precipitate by pouring strong hydrochloric acid through the filter; if there is only a little precipitate, place the beaker at once under the funnel and dissolve all the precipitate on the filter. Wash the filter thoroughly with hot dilute, hydrochloric acid. Add to the solution the sulfuric and oxalic acid solution that was previously obtained by dissolving the stain on the platinum dish. Evaporate on the steam bath to remove free chlorine and until the volume of liquid is small; the color of the solution may

be yellow from a little dissolved ferric chloride, or more or less yellowish green if nickel is present.

When much nickel is present, the treatment of the solution, after the removal of the greater part of the iron by shaking with ether, should be carried out as described on page 197.

To remove, now, small quantities of iron that escaped solution in ether (when the operation was properly carried out this should amount to only a few milligrams) nearly neutralize the free acid by the addition of ammonia but do not continue adding ammonia until a permanent precipitate is formed. To the barely acid solution, add 1 or 2 cc. of 20 per cent. ammonium acetate solution and heat just to boiling. Filter off the reddish-brown flocks of basic ferric acetate through a small filter and wash well with hot water. If the precipitate is at all bulky, dissolve it in hydrochloric acid and repeat the basic acetate separation exactly as before.

Combine the filtrates from the basic acetate precipitation, make slightly acid with acetic acid and saturate the cold solution with hydrogen sulfide gas. Without interrupting the current of hydrogen sulfide, slowly heat the solution to boiling, then turn out the flame and allow the solution to cool while hydrogen sulfide is constantly passing through it. After the precipitated nickel and cobalt sulfides have settled, filter and wash carefully with water. Concentrate the filtrate in a porcelain dish; often during this evaporation some more nickel sulfide precipitates out. Transfer the solution to a beaker and once more introduce hydrogen sulfide. After filtering off any nickel sulfide that may have formed, evaporate to expel hydrogen sulfide.

Transfer the solution containing the manganese to a 400-cc. beaker, dilute to about 200 cc. and neutralize with ammonia. Add a little bromine water and a slight excess of ammonia. Heat the liquid and stir to facilitate the formation of the manganese dioxide precipitate. By adding more bromine and making slightly ammoniacal again, make sure that the precipitation of the manganese was complete. In case an appreciable quantity of precipitate was formed the last time, repeat the operation.

After allowing to stand a short time on the water bath, filter the liquid through an ashless paper and wash the precipitate a few times with hot water. Test the filtrate for manganese by

treatment with bromine and ammonia and, in case no precipitate forms, evaporate the liquid to dryness, which sometimes causes the deposition of small quantities of manganese dioxide.[1]

It is a quite common practice among chemists to ignite and weigh this precipitate, calling it Mn_3O_4. According to the quantity of precipitate and the ignition temperature, however, the oxygen content varies somewhat so that it is better to convert it into either pyrophosphate or sulfate. In either of the latter forms, the composition of the ignited precipitate is constant and the results obtained are exact.

To convert the manganese dioxide precipitate into pyrophosphate, dissolve it in hot, dilute hydrochloric acid to which a few cubic centimeters of sulfurous acid have been added. Pour the acid through the filter and wash the latter thoroughly with hot water. Dilute the solution to 100 cc., add 20 g. of ammonium chloride, 5 to 10 cc. of a cold, saturated solution of disodium phosphate and ammonia, drop by drop, until a slight excess is present. Heat to boiling and keep at this temperature for 3 or 4 minutes, or until the precipitate assumes a silky crystalline appearance. Allow the solution to cool.

When a precipitate can be dried easily and completely at a temperature not far from the boiling point of water it used

[1] In a dilute acid solution bromine has scarcely any oxidizing effect upon manganous ions. In other words the reaction:

$$Mn^{++} + Br_2 + 2H_2O \rightleftarrows MnO_2 + 2Br^- + 4H^+$$

reaches an equilibrium before little, if any, of the manganese is precipitated. On the other hand, when the acid is neutralized the equilibrium of the above reaction is disturbed and the precipitation of the manganese as dioxide may be made quantitative. Ammonia is used in the above test as a neutralizing agent. Bromine, however, also reacts directly with ammonia and oxidizes a part of its nitrogen to free nitrogen in the sense of the following equation:

$$8NH_3 + 3Br_2 = 6NH_4Br + N_2$$

This reaction often goes a little farther and part of the ammonium salt is oxidized, leaving the solution slightly acid;

$$2NH_4^+ + 3Br_2 \rightleftarrows N_2 + 6Br^- + 8H^+$$

Although this last reaction takes place only to a slight extent, it is clear that, as a result of the two last reactions, the precipitation of the manganese is made more difficult. This is the reason for the repeated treatment with bromine and ammonia.

to be common practice to filter it upon a weighed (*tared*) filter. Gooch, however, proposed the use of a perforated crucible containing a felt of asbestos fibers to serve as filtering medium. This has two advantages: first, the crucible may be dried at a temperature much higher than could be used with a paper filter; second, suction can be used during filtration and considerable time saved. If the asbestos felt is properly prepared and the crucible is dried originally to constant weight at the temperature to which the precipitate is to be heated, the results are as good as those obtained by any other method.

To prepare the asbestos felt, first digest the asbestos fibers, in pieces about 0.5 cm. long, for about an hour on the water bath with strong hydrochloric acid. Collect the asbestos upon a filter plate and wash out all the acid with water. Shake it up in a bottle with water so that a thin suspension is formed. Stretch a piece of "bill-tie" rubber tubing over a funnel, Fig. 122, and place the crucible, *T*, in the opening.[1] The funnel should be large enough so that the crucible is suspended by the rubber without touching the sides of the funnel. Pour enough of the asbestos suspension into the crucible, applying gentle suction, to produce a layer 1 or 2 mm. thick. Place a small filter plate upon this layer and pour a little more asbestos into the crucible. Pour water through the crucible until no more asbestos fibers are washed away. To see the fibers pour the liquid into a small beaker and hold it up to the light.

Instead of using an asbestos felt, Munroe,[2] Neubauer and others have recommended the use of platinum sponge. To prepare such a felt, place the perforated crucible upon several layers of filter paper and pour into it a mixture of ammonium chloroplatinate crystals ground up with a little alcohol. Heat the

[1] Instead of using the flat rubber band to support the crucible, L. H. Bailey has devised a Gooch crucible holder which is shown in Fig. 122*a*. It is made of rubber and fits an ordinary 2-in. glass funnel. The funnel is inserted in a perforated rubber stopper which in turn fits the suction flask. The upper edge of the holder projects over the upper edge of the funnel and the lower edge of the holder rests on the side of the funnel. When suction is applied the holder fits tightly to the funnel.

[2] C. E. Munroe, J. anal. Chem., **2,** 241; Chem. News, **58,** 101; W. O. Snelling, J. Am. Chem. Soc., **31,** 456 and O. D. Swett, *ibid*, **31,** 928. The last reference gives a table of suitable solvents for removing ignited precipitates.

crucible carefully and shape the felt to the bottom of the crucible, finally burnishing it slightly with the aid of a glass rod of suitable shape.

The manganese ammonium phosphate precipitate may be filtered off through a washed filter, ignited very carefully in a platinum crucible and weighed as manganese pyrophosphate. It is fully as satisfactory, however, to use either the Gooch or Munroe crucible. First, dry the crucible half an hour at about 130° and then ignite it in an electric furnace, or within a larger

FIG. 122.

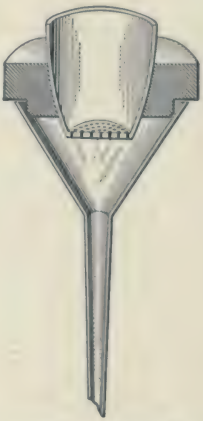

FIG. 122*a*.—Sectional view of Bailey's Gooch crucible holder with funnel and crucible.

crucible heated by a gas flame. In this way there is no danger of gases from the flame coming in contact with the asbestos or platinum felt. After igniting at a high temperature for about 10 min., allow the crucible to cool in the air somewhat[1] and then let it remain half an hour in a desiccator before weighing.

[1] If the very hot crucible is placed immediately in a desiccator with a tightly fitting cover, the expansion of the air causes the top of the desiccator to jump up and down several times and then, on cooling, a partial vacuum is produced in the desiccator. As a result the crucible cools very slowly. If weighed while still warm, it will weigh too little, owing to air currents rising from the balance pan. Much time is saved, therefore, by allowing the crucible to cool somewhat before placing it in the desiccator.

Filter off the manganese ammonium phosphate using either the weighed Munroe or Gooch crucible, and wash the precipitate thoroughly with a cold, 10 per cent., solution of ammonium nitrate. Dry the crucible and its contents for at least half an hour at about 130° and then gradually raise the temperature until finally a high heat is obtained. During this last heating the manganese ammonium phosphate is changed to manganese pyrophosphate:

$$2MnNH_4PO_4 = Mn_2P_2O_7 + 2NH_3 + H_2O$$

It is very important not to ignite the precipitate too quickly, as in that case the ammonia acts upon the phosphate, reducing it and turning it very black; it is a very tedious operation to whiten such a precipitate by ignition.

To convert the manganese dioxide precipitate into sulfate, ignite it with the filter in a weighed porcelain crucible, cover the crucible with a watch-glass, and dissolve the precipitate in hydrochloric acid (sp. gr. 1.12). Heat carefully until the chlorine is expelled and add, for each 0.1 g. of precipitate, about 0.5 cc. of dilute sulfuric acid (1 : 5). To remove the excess of the latter, heat the crucible and its contents in an air bath, which may be prepared according to the suggestion of Gooch and Austin,[1] with the aid of a larger porcelain crucible.[2] The outer crucible (Fig. 123), is chosen of such a size that when the smaller crucible is placed within it, and suspended by a piece of asbestos cord wrapped around it, or by means of a small triangle, the distance between the walls of the two crucibles is about 1 cm. on all sides.

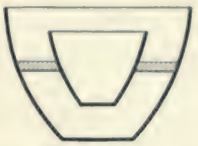

FIG. 123.

Heat the outer crucible for a short time with a good Bunsen flame, cool and weigh. Continue the heating until a constant weight is obtained. The manganese sulfate should be pale pink, not brown at the bottom, and should be perfectly soluble in water.

[1] Z. anorg. Chem., **17**, 264 (1898).

[2] If an electrically-heated drying oven is available, heat the crucible in it to constant weight at 450°–500°.

Computation.—If p_1 is the weight of manganese pyrophosphate and s the weight of substance taken, then

$$\frac{2\text{Mn} \times p_1 \times 100}{\text{Mn}_2\text{P}_2\text{O}_7 \times s} = \frac{38.70p_1}{s} = \text{per cent. Mn}$$

If p_2 is the weight of the manganese sulfate and s the weight of substance taken then

$$\frac{\text{Mn} \times p_2 \times 100}{\text{MnSO}_4 \times s} = \frac{36.38p_2}{s} = \text{per cent. Mn}$$

The method can be modified to advantage in the analysis of special materials:

(*a*) *Alloys Rich in Manganese.*—(Ferro-manganese, metallic manganese, etc., which contain only little iron). Dissolve from 2 to 4 g. of the metal[1] in nitric acid, decompose the nitrates and remove the silica[2] as described above. Carefully add ammonia to the filtrate from the silica until the solution is neutral, add ammonium acetate, and carry out a basic acetate separation (*cf.* p. 191). If there is a considerable precipitate of basic ferric acetate, redissolve it and repeat the precipitation. Make the entire filtrate slightly acid with acetic acid and precipitate the copper, nickel and cobalt with hydrogen sulfide. Transfer the filtrate to a calibrated 250 cc. flask, when it is at the laboratory temperature, make up to the mark and thoroughly mix by pouring back and forth several times into a dry beaker. By means of a 50 cc. pipette, take an aliquot part for the manganese determination.[3]

[1] As regards the necessity for getting a representative sample, see page 41 of this book.

[2] In the dehydration of the silicic acid, the dish should not be overheated or there is danger of losing some manganous chloride by volatilization.

[3] To avoid error in taking the aliquot part, it is necessary to make sure that the pipette and calibrated flask are properly calibrated. This is particularly necessary because several temperatures have been suggested as standards for calibration purposes and, moreover, both flasks and pipettes are calibrated in two ways—for contents and for delivery. In this case, the flask should be calibrated for contents and the pipette for delivery. A simple way to test the flask is to take some water that is at the room temperature and add the contents of the 50 cc. pipette 5 times to the dry flask. In using the pipette, allow the pipette to flow freely and when the liquid stops flowing, touch the sides of the flask, or the surface of the liquid, with the point of the pipette to

The determination of the manganese can now be carried out in the same way as before. In some cases, however, calcium is likely to be present and then the manganese dioxide precipitate will contain some of this element.[1] It is better, then, to precipitate the maganese as sulfide by passing hydrogen sulfide into the slightly ammoniacal solution. The manganese sulfide is easily converted into sulfate (*cf.* p. 195).

(*b*) *Alloys Rich in Nickel.*—(Nickel steel with high nickel content, chrome-nickel steel, etc.). To avoid the difficulties involved in precipitating considerable nickel in the presence of manganese, due to the fact that the solubility products of nickel and manganese sulfides lie comparatively near together, it is better to remove most of the nickel, after shaking out the ferric chloride with ether, in the following manner: Evaporate the hydrochloric acid solution to dryness, taking care not to set fire to the ether it contains, take up the residue in hydrochloric acid and neutralize the excess of acid with ammonia. Add bromine, make slightly ammoniacal again and heat. By this treatment, the greater part of the nickel remains in solution forming a blue liquid, and the manganese together with the remainder of the iron and some nickel is contained in the precipitate. Filter off the brown precipitate and again test the

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remove another drop, and then take away the pipette (do not blow through it). Place a mark on the neck of the flask where the bottom of the meniscus comes. It is best to dry the flask again and repeat the operation. It makes no difference now, whether the 250 cc. flask or the pipette has been correctly calibrated because it is known that the pipette will deliver exactly one-fifth of the solution in the flask. It is important, however, to make sure that the solution has the same temperature when made up to the mark that it has when the aliquot part is taken. If the solution is warm when made up to the mark and cools during the pouring back and forth into the beaker, then the results will come out too high and conversely.

If there is a balance in the laboratory capable of weighing 1 kg. and sensitive to a centigram, it is more accurate to use it for dividing the solution. Weigh the perfectly dry flask, together with its ground glass stopper, and then weigh it again with the solution in it, without taking special pains to bring it exactly to any specified volume. Thoroughly mix the solution and pour a part of it into another weighed flask. Stopper this flask and again weigh it. From the ratio between the two weights of the solution the corresponding fraction of the weight of sample taken for analysis can be computed.

[1] *cf.* Reis, Z. angew. Chem., **1892**, 672.

filtrate for manganese by treatment with bromine and ammonia. Dissolve the precipitated oxides on the filter by treating with hydrochloric acid[1] (sp. gr. 1.12), add a little sulfuric acid, and evaporate the solution on the Finkener tower until fumes of sulfuric acid are evolved. Fuse the residue with sodium hydroxide and either sodium peroxide or potassium chlorate and thus remove the remainder of the iron and nickel by the method described on p. 189. Eventually determine the manganese as sulfate or pyrophosphate.[2]

(*c*) *Materials Insoluble in Acid.*—(Ferro-chrome, ferro-tungsten, silico-manganese, etc.).

Such materials can be attacked by the method described on p. 178 for the determination of silicon. It is usually advantageous to use the sodium carbonate and magnesia mixture in the proportions suggested by Rothe.

Weigh out from 0.5 to 2 g. of substance, according to the probable manganese content, ignite it with sodium carbonate and magnesia, transfer the ignited mass to an agate mortar, moisten it with water and rub it up with the pestle to as thin a paste as possible. Rinse into a beaker, dilute with hot water to a volume of about 200 cc. and reduce the manganate by adding a little sodium peroxide. After destroying the excess of peroxide by boiling the liquid, allow the precipitate to settle, decant off the supernatant liquid through a filter and wash several times by decantation, taking pains to keep the precipitate off the filter as far as possible.

Finally, dissolve the washed precipitate in the beaker by the addition of hydrochloric acid (sp. gr. 1.12), add to the solution the filter with the small deposit of manganese dioxide upon it, and heat to expel chlorine. Filter off the filter paper shreds and any unattacked material and wash the filter with water containing hydrochloric acid. If some unattacked material is found (this usually collects in the bottom of the beaker in the form of small black particles, having a gritty feeling when pressed upon with

[1] If the precipitate remains on the filter very long, it may be necessary to add a little sulfurous acid to the hydrochloric acid.

[2] If phosphorus and manganese are not present to an appreciable extent, the fusion with sodium hydroxide and peroxide may be omitted. The iron and nickel are then removed in the usual way.

a glass stirring rod) burn the filter in a platinum dish and fuse the ash with sodium carbonate. Take up the product of the fusion with water and add sodium peroxide to reduce the manganate, if any is shown to be present by the green color of the aqueous extract. Filter off the precipitate of manganese and ferric oxides, etc., add the filtrate to that obtained from the fusion with sodium carbonate and magnesia, and add the hydrochloric acid solution of the precipitate to the main hydrochloric acid solution.

The alkaline solution thus obtained may be used for the determination of phosphorus or chromium.

Evaporate the hydrochloric acid solution of the precipitate containing the manganese to dryness in a porcelain dish and heat for some time to 135° over an asbestos plate. After cooling, take up in hydrochloric acid and remove the silica as described on p. 170.

Dilute the filtrate from the silica to about 250 cc., neutralize the free acid by the addition of ammonia, add ammonium acetate and precipitate the iron as basic ferric acetate, as described on p. 191. Usually it is advisable to carry out a second basic acetate separation.

Make the filtrate distinctly acid with acetic acid and introduce hydrogen sulfide to precipitate any nickel present. Filter off the nickel sulfide, catching the filtrate in a 300 cc. beaker, and precipitate the manganese by the addition of bromine and ammonia (*cf.* p. 191). The precipitation may be hastened by vigorous stirring.

Filter off the precipitate, wash it well with water, and preserve the filtrate in order to test it for manganese. Transfer, by means of a stream from the wash bottle, as much as possible of the precipitate to a beaker, place the beaker under the funnel and pour hydrochloric acid (sp. gr. 1.12) through the filter. Wash the filter thoroughly and heat the acid to dissolve the manganese dioxide. Concentrate the solution until the volume is very small and precipitate the manganese as sulfide, using freshly prepared ammonium sulfide[1] as reagent.

To carry out the precipitation, take 50 to 100 cc. of ammonium

[1] To prepare ammonium sulfide free from polysulfide, saturate ammonia water (sp. gr. 0.96) with hydrogen sulfide and then add an equal volume of ammonia water.

sulfide solution (according to the quantity of manganese present), and heat it just to boiling in a 300–400 cc. beaker. Heat the manganese solution, which must be as nearly neutral as possible, and pour it into the hot ammonium sulfide solution. Rinse out the beaker that contained the manganese solution and heat the liquid a short time in order to obtain a precipitate of green manganese sulfide that will filter well.

After allowing all the precipitate to settle, pour the liquid through a filter that runs well[1] and wash the precipitate with hot water containing a little ammonium sulfide. Evaporate the filtrate and washings and recover any manganese that it may contain by treatment with bromine and ammonia. This treatment with bromine and ammonia should be repeated to be sure that all manganese has been precipitated.

Ignite the manganese sulfide precipitate in a weighed porcelain crucible, dissolve the resulting manganomanganic oxide in hydrochloric acid (sp. gr. 1.12) and convert it into the anhydrous sulfate as described on p. 195. The small quantity of manganese dioxide recovered from the filtrates may be ignited separately and weighed as Mn_3O_4.

(*d*) *Shortening the Time Required.*—The time required for the analysis may be shortened considerably up to the point of the ether separation, by using a round-bottomed flask instead of porcelain casserole for dissolving the sample. For samples weighing from 5 to 10 g., a flask of about 500 cc. capacity is suitable, or a 300 cc. flask for a 3 g. sample.

Weigh the sample directly into the flask, dissolve it by the gradual addition of the necessary quantity of nitric acid (sp. gr. 1.18) heat over a small flame until solution is complete, and evaporate over a free flame while keeping the flask in constant motion. Hold the flask by a clamp attached to the neck.

[1] If the precipitate at first runs through the filter, continue to filter (provided the liquid does not run too slowly through the filter), and eventually transfer all the precipitate to the paper. As soon as the filtrate begins to run through clear, change the vessel under the funnel and pour the turbid filtrate through the filter again. In filtering keep the filter nearly filled all the time and do not wait for all the liquid to run through during the washing. Otherwise, the manganese sulfide oxidizes on the filter, dissolves in the wash water, and a precipitate of manganese sulfide is formed again in the filtrate which contains ammonium sulfide.

When the solution has been evaporated to dryness, heat carefully to decompose the nitrates, allow to cool, dissolve the oxides in the necessary quantity of concentrated hydrochloric acid (sp. gr. 1.2) again evaporate to dryness, and continue the heating until the color of the residue is dark brown but not necessarily until it becomes red. Cool, dissolve in concentrated hydrochloric acid and heat until there is no ferric oxide visible in the bottom of the flask. Dilute and filter off the silica. Transfer the solution to the flask again and evaporate until it is ready for treatment with ether.

This method of working is not suitable when it is desired to determine the silicon because it is difficult to remove the last traces of silica from the flask.

Test Analyses.—To test the method described for the separation of manganese from iron, 25 cc. of a manganous chloride solution, containing 0.0354 g. of manganese, were mixed with pure ferric chloride solution, corresponding to about 3.5 g. of iron, and the manganese determined. The average of three closely-agreeing analyses gave 0.0364 g. of manganese when weighed as Mn_3O_4 and 0.0354 g. of manganese when weighed as $MnSO_4$.

Accuracy of the Results and Permissible Deviation

Besides errors in weighing, certain other unavoidable errors arise which in careful work should not be large. In general, if the manganese is weighed as sulfate or as pyrophosphate, the weight of the final precipitate should be accurate within 1 mg. when the precipitate weighs 50 mg. or less and within 2 mg. with larger quantities. According to the amount of material taken for analysis (*e.g.*, 5 g. when less than 2 per cent. of manganese is present and 1 g. otherwise) this will correspond to the following permissible deviations in duplicate results:

From	To	Deviation
0.0 per cent.	0.2 per cent.	± 0.01 per cent.
0.2 per cent.	1.0 per cent.	± 0.02 per cent.
1.0 per cent.	5.0 per cent.	± 0.04 per cent.
5.0 per cent.	10.0 per cent.	± 0.06 per cent.
10.0 per cent.	30.0 per cent.	± 0.08 per cent.
30.0 per cent. upward		± 0.10 per cent.

Applicability of the Method.—Satisfactory results are obtained in the analysis of iron, steel, and other alloys pertaining to the steel industry.

2. VOLUMETRIC DETERMINATION OF MANGANESE

A number of excellent volumetric methods have been proposed for the determination of manganese in iron and steel. These methods are of three types: (1) the direct titration of a manganous salt with potassium permanganate; (2) the precipitation of the manganese as dioxide, solution of the precipitate in a known amount of ferrous salt, and titration of the excess of the latter with a suitable oxidizing agent; (3) oxidation of the manganese to permanganate, addition of a known amount of reducing agent, and titration of the excess of the latter. Potassium permanganate is commonly used for the final titration in all these methods but the value of 1 cc. of the solution in terms of manganese is different in each case.

The first type of method has always been a favorite one in Germany and there are over fifty publications concerning it in scientific journals since 1879. It is the only volumetric method mentioned in the German edition of this book but it has seemed best to mention, in the English text, at least one representative method of each of the other types.

(a) Modified Volhard Method

Principle.—Manganous salts react with permanganate in accordance with the following equation:

$$2MnO_4^- + 3Mn^{++} + 2H_2O = 5MnO_2 + 4H^+$$

Gorgeu[1] first attempted to use this reaction as a basis for the volumetric determination of manganese but Volhard is generally considered to be the father of the method in its present form.[2]

The conditions necessary to carry out the reaction strictly in accordance to the above equation, in the analysis of a solution

[1] Ann. chim. phys., III, **66,** 154 (1862).
[2] Deiss, Chem. Ztg., **34,** 237 (1910).

of manganous salt containing a large quantity of ferric chloride, are obtained most readily by precipitating the iron from a hot, dilute solution with a slight excess of zinc oxide, adding quickly an excess of potassium permanganate, and titrating the excess of the latter in a suitable manner.

If the conditions are not quite right it is possible that the reaction between the manganous salt and the permanganate may take place differently. Thus, for example, in Wolff's[1] method where the permanganate is added gradually after the iron has been precipitated by the zinc oxide, less permanganate is required to precipitate all the manganous salt, and, within certain limits, the volume of permanganate required is smaller in proportion as the amount of zinc oxide added is large. In some cases the error may amount to 10 per cent. of the total manganese content.

If the zinc oxide excess is equal to zero, so that only ferric hydroxide is present (a condition difficult to fulfil) then the permanganate consumption by the Wolff method corresponds to that required by the equation.

The reason for low results when an excess of zinc oxide is used is chiefly due to the fact that some of the manganese is precipitated with the ferric hydroxide.

When the titration of the manganous salt by permanganate is carried out in a slightly *acid* solution, as recommended by Volhard, the results are lower than the equation demands. In this case the error is due chiefly to the fact that the manganese dioxide precipitate, as it forms slowly, carries with it some adsorbed manganous oxide and thereby escapes reaction with the permanganate.

In the modification suggested by Schöffel and Donnath, the manganous chloride solution containing suspended ferric hydroxide, formed by the addition of an excess of zinc oxide, is added to an excess of permanganate solution; correct results may be obtained if the two solutions are mixed quickly enough. The condition of having permanganate always present in excess is not alone sufficient to prevent disturbances such as are likely to result in the method of Volhard and Wolff.

In using the Wolff method it is often proposed to avoid error

[1] Stahl u. Eisen, **1884,** 702; **1891,** 377.

by using an empirical factor for the permanganate solution instead of the theoretical value as established by equations. Since, however, the factor varies with the amount of zinc oxide added to precipitate the iron, it is evident that this method is not altogether satisfactory.

Probably the most successful expedient, and one that gives good results in the hands of a skilful worker, is to standardize the permanganate solution against a manganous solution of known content in exactly the same way in which the analysis is to be carried out.

Requisite Apparatus and Solutions.—In carrying out the titrations, it is convenient to have at hand a wooden frame, Fig. 124, fitted to hold in an inclined position two flasks of 1.1 to 1.5 liters capacity. The hollows in which the bottoms of the flasks rest are covered with felt to prevent breakage. In carrying out a titration, the frame is placed upon the working bench so that the middle of the flask is at about on a level with the eye, in such a way that there is a background of a window on which the sun is not shining.

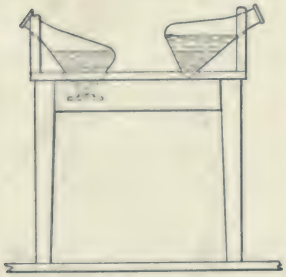


Fig. 124.

For the titration, the following solutions are used:

1. *Potassium Permanganate Solutions.*—It is well to have two solutions of permanganate on hand, a weaker solution containing about 16 g. of potassium permanganate in 5 liters of water and a stronger one containing about 40 g. of the permanganate in the same volume of solution.

The solutions are prepared by dissolving weighed portions of pure potassium permanganate in a beaker using distilled water that has been recently boiled and allowed to cool.[1] The solution is decanted off from time to time into a clean 5-liter flask and eventually diluted up to the mark. Before using them for titrations, the permanganate solutions should stand in stoppered bottles for from eight to fourteen days, protected from light and

[1] The addition of 10 g. caustic potash per liter retards the decomposition of permanganate by dust, reducing gases, or precipitated manganese dioxide. W. Blum, J. Am. Chem. Soc., **34**, 1379.

dust. At the end of this time any oxidizable matter in the solution will have reacted with the permanganate and any manganese dioxide present as colloid in the freshly prepared solutions will have deposited on the bottom or sides of the bottle in the form of a brown precipitate. The solutions should then be filtered through asbestos. If protected from light and dust (filtering the air entering the bottle through alkaline permanganate) the filtered solution will keep indefinitely.[1]

2. *Sodium Arsenite Solutions.*—The strength of two arsenite solutions are chosen preferably so that 1 cc. of permanganate is equivalent to about 2 cc. of arsenite. To prepare the weak and strong solutions, weigh portions of 8 and 20 g. of pure arsenic trioxide into beakers containing half as much pure sodium hydroxide. Dissolve in a little water, with heating, filter if necessary, and dilute each solution to a volume of 5 liters.

Standardization of the Permanganate Solutions

(*a*) *Against Sodium Oxalate.*—The standardization of potassium permanganate solutions by means of pure sodium oxalate, $Na_2C_2O_4$, has been shown to give reliable results by a number of chemists and is recommended by the United States Bureau of Standards. According to the strength of the permanganate, weigh out about 0.3 or 0.8 g. of the pure, anhydrous salt and dissolve it in 500 cc. of boiling water. Add 50 cc. of dilute sulfuric acid (1 : 5) and titrate while the solution is hot.

It is important, in this titration, that the initial temperature of the solution should be between 80° and 90° and the final temperature above 60°. The titration must take place slowly, especially at the start and finish. Otherwise too much permanganate is required.

The reaction that takes place in the titration may be expressed as follows:

$$2MnO_4^- + 5C_2O_4^{--} + 16H^+ = 2Mn^{++} + 10CO_2 + 8H_2O$$

Thus, 2 molecules of permanganate will oxidize 5 molecules

[1] *cf.* Morse, Hopkins and Walker, Am. Chem. J., **18,** 401; Gardner and North, J. Soc. Chem. Ind., **23,** 599; Warynski and Tscheischwili, J. chim. phys., **6,** 567; Treadwell-Hall, Quantitative Analysis, II, 603 (1914).

of oxalate and we have seen that 2 molecules of permanganate oxidize 3 molecules of manganous salt to manganese dioxide. Five moles of sodium oxalate (670.0 g.) are equivalent, therefore, to 3 moles of manganous salt (164.79 g. of manganese).

If a g. of sodium oxalate require n cc. of permanganate, then

$$1 \text{ cc. } KMnO_4 \text{ soln.} = \frac{164.8 \times a}{670.0 \times n} = 0.2460 \frac{a}{n} \text{ g. Mn}$$

This factor applies only to the Volhard method.[1]

(*b*) *Against Sodium Thiosulfate Solution.*—When potassium permanganate is added to an acid solution of potassium iodide, the following reaction takes place:

$$2MnO_4^- + 10I^- + 16H^+ = 2Mn^{++} + 8H_2O + 5I_2$$

and the free iodine may be titrated with sodium thiosulfate.

$$I_2 + 2S_2O_3^{--} = 2I^- + S_4O_6^{--}$$

If the strength of either the permanganate or of the thiosulfate solution is known, that of the other solution may be computed.[2] The reaction furnishes a rapid and accurate method of standardization.

Dissolve about 2 g. of pure potassium iodide in 300 cc. of water, add 5 cc. of dilute hydrochloric acid (sp. gr. 1.12) and if the solution is at all yellow (free iodine liberated by iodate in the iodide or of free chlorine in the acid) carefully discharge the color by the addition of a drop or more of dilute thiosulfate solution. Add to the colorless solution of potassium iodide an accurately measured volume of the permanganate solution, using 50 cc. in the case of the weaker solution and 25 to 30 cc. of the stronger. The solution is at once colored red by the liberated iodine.[3] In case a precipitate of manganese dioxide is formed, dissolve it by the addition of a little more hydrochloric acid. Titrate the solution with tenth-normal sodium thiosulfate until

[1] Ann., **198,** 333, **242,** 98 (Volhard).

[2] It is possible to prepare perfectly pure, anhydrous thiosulfate (*cf.* Young, J. Am. Chem. Soc., **26,** 1028) and with this salt it is easy to prepare a tenth-normal solution.

[3] The iodine really unites with unchanged iodide ions to form I_3^- ions in which two-thirds of the iodine behaves like free iodine.

nearly colorless, then add a little starch solution[1] and finish the titration.

Computation.—The above equations show that 2 molecules of permanganate liberate 10 atoms of iodine which in turn react with 10 molecules of thiosulfate. In the titration of the manganous salt by permanganate, we have seen that 2 molecules of permanganate react with 3 molecules of manganous salt. Thus, 3 atoms of manganese in the bivalent condition have the same reducing power as 10 molecules of thiosulfate and 1 cc. of tenth-normal thiosulfate is equivalent to $\frac{3 \times \text{Mn}}{10 \times 1000} = 0.3 \times 0.05493 =$ 0.001648 g. Mn. If, in the standardization, n cc. of tenth-normal thiosulfate are equivalent to a cc. of permanganate

$$1 \text{ cc. } KMnO_4 \text{ solution} = 0.001648 \frac{n}{a} \text{ g. Mn.}$$

The results obtained by this method of standardization agree closely with those obtained by standardizing against sodium oxalate. There is little choice between the two methods. The standardization of the arsenite solutions is explained in the description of the method of analysis.

Method of Carrying Out the Analysis

(*a*) *Preparation of the Sample for the Titration.*—If the manganese alone is to be determined in an alloy containing less than 10 per cent. of this element, proceed in the following manner:

Weigh out 3 separate portions,[2] each containing 2 g. of material, into a porcelain dish of 12 cm. diameter. Cover the dish with a watch-glass and dissolve each sample by the gradual addition of 25 cc. of nitric acid (sp. gr. 1.18). When solution is complete, remove the watch-glass, evaporate to dryness, and destroy the nitrates by igniting at first over asbestos and finally over the free flame until no more nitrous fumes are evolved. Cool and take up the residue in about 20 cc. of concentrated hydrochloric acid (sp. gr. 1.2).

[1] Zinc-iodide-starch solution can be bought which is suitable for such titrations or a starch solution may be prepared by dissolving 0.5 g. of soluble starch in 25 cc. of hot water.

[2] One sample is to be used for a preliminary titration which does not, as a rule, give exact results.

If a dark-colored residue (containing graphite) remains undissolved, evaporate the hydrochloric acid solution to dryness, dehydrate any silicic acid by heating to 135°, redissolve in hydrochloric acid, dilute, filter and wash the residue thoroughly before proceeding with the titration. The undivided solution is used.

If graphite is not present, it is unnecessary to filter off the silica. Evaporate the hydrochloric acid solution of the oxides to dryness, to remove any chlorine that may have been formed from the interaction of manganomanganic oxide and hydrochloric acid, take up the residue in hydrochloric acid (sp. gr. 1.12) and rinse the solution into an Erlenmeyer flask of about 1 liter capacity. The solution is now ready for titration.

If it is desired to combine the manganese determination with the determination of silicon, or phosphorus in samples rich in phosphorus, or nickel in a nickel steel, a larger quantity of material may be taken for the analysis and an aliquot part of the solution used for the manganese determination. In this way a better average sample is obtained. Of materials containing up to 10 per cent. manganese, from 8 to 10 g. are taken, of richer manganese alloys (ferro-manganese, metallic manganese, etc.) a correspondingly smaller amount (down to 2 g.). Dissolve the sample in nitric acid (sp. gr. 1.18) and remove the silica as described on p. 173.

Catch the filtrate from the silica in a 500 cc. calibrated flask, or, if the weight taken was less than 8 or 10 g., in a 250 cc. flask. If a dark colored residue remains after volatilization of the silicon by treatment with sulfuric and hydrofluoric acids, dissolve it in the crucible with a little hydrochloric acid (sp. gr. 1.12) and rinse the solution into the calibrated flask.

Fill the flask up to the mark with water which is at the laboratory temperature, thoroughly mix by pouring back and forth into a dry beaker several times, and take an aliquot part for the manganese determination by means of a pipette, a smaller calibrated flask, or by weighing.

If the substance for analysis is insoluble in acids, ignite from 2 to 3 g. with magnesia and sodium carbonate as described for the determination of silicon, p. 178. Transfer the ignited mass from the crucible to an agate mortar, moisten with water, break up the larger pieces with the pestle and grind into a fine powder.

Rinse the mass into a beaker, cover the latter with a watch-glass and add a little sodium peroxide to decompose any manganate that was formed during the ignition. Heat the liquid on the water bath, with frequent stirring, until the excess of peroxide is decomposed and, if the solution then appears green or violet (from manganate or permanganate), repeat the treatment with sodium peroxide. After the manganate has all been reduced, the solution should be colorless, or yellow in case chromium is present. Filter off the precipitate, containing all the manganese and iron together with the magnesia, etc., and wash it well with hot water. Rinse the precipitate into a porcelain dish and dissolve it in hydrochloric acid (sp. gr. 1.12). Evaporate the solution nearly to dryness, to make sure that all the chlorine is expelled, and rinse with dilute hydrochloric acid into a 250 cc. calibrated flask. Make up to the mark with water and take an aliquot part for the titration.

The quantity of manganese to be titrated determines which of the two permanganate solutions should be used. In general, solutions containing from 40 to 80 mg. of manganese (corresponding to a 2 g. sample with 2 to 4 per cent. manganese) may be titrated with the weaker solution; if the manganese content is higher the stronger solution should be used.

If the sample contained only a little iron, add enough pure ferric chloride to each solution before titration so that the iron content will correspond to about 1 g. of metal. For this purpose, it is well to have at hand a solution of ferric chloride made by dissolving about 500 g. of pure ferric chloride ($FeCl_3 + 6H_2O$) in water with a little hydrochloric acid and diluting to 1 liter; such a solution contains about 1 g. of iron in 10 cc.

(*b*) *Titration of the Solution.*—The solution to be titrated, prepared as just described, should be in an Erlenmeyer flask of about 1 liter capacity. To oxidize traces of ferrous salt that may be present, add a small crystal of potassium chlorate, or, better, a few drops of pure, concentrated hydrogen peroxide solution[1] and boil gently for 10 or 15 min. to destroy the excess of oxidizing agent (replacing the hydrochloric acid lost by evaporation). There should be no odor of free chlorine.

Meanwhile heat the distilled water necessary for the titra-

[1] Perhydrol.

tion to boiling in a 2 liter flask and triturate the zinc oxide necessary for the precipitation of the iron in a mortar with water, until a thin paste is obtained. This may be kept in a small Erlenmeyer flask. If the approximate manganese content of the solution is not known, determine it by a trial titration carried out in the following manner:

Dilute the manganese solution in the Erlenmeyer flask with boiling water until the volume is about 600 to 700 cc. Add the suspension of zinc oxide in small amounts until, after vigorous shaking, all the iron is precipitated in the form of brown ferric hydroxide[1] and the solution is clear and colorless after the precipitate settles.

For convenience, place the flask in an inclined position in the support described on p. 204 while the precipitate is settling. Add 10 cc. of the permanganate solution from a burette, shake vigorously and replace the flask upon the support. If, when the precipitate settles, the supernatant liquid is uncolored by permanganate, add another 10 cc. of permanganate, shake and again allow to settle. Repeat the operation until the solution above the precipitate is colored by permanganate. Then add the corresponding arsenite solution in small quantities, shaking and allowing to settle after each addition. Continue to add arsenite solution until the permanganate is decolorized.

From the volumes of permanganate and arsenite solutions used in this trial titration, the approximate volume of permanganate required can be computed by assuming the two solutions to be of the same strength. The exact value of the arsenite solution is determined at the time the accurate titration is made.

For this accurate titration of the manganese content of the solution, measure from a burette, into a small beaker, from 2 to 4 cc. of permanganate more than that found necessary by the trial titration. Then dilute the manganese solution containing ferric iron to a volume of 600 to 700 cc., add the necessary quantity of zinc oxide suspension, and shake well. When all the iron is precipitated, quickly add the permanganate solution from the

[1] It is not necessary to add zinc oxide until the excess whitens the precipitate. There is no danger of an excess of zinc oxide doing any harm, however, provided the permanganate solution is added rapidly, as in the main analysis.

beaker, rinse the beaker, and shake the contents of the flask vigorously.

If the solution should now be colorless, or show only a very pale permanganate color, it is best to repeat the experiment using a somewhat larger quantity of permanganate.

To determine the excess of permanganate, add the arsenite solution in small portions from a burette, shaking and allowing to settle each time, until the supernatant solution is colorless. It is necessary, toward the last, to add but a drop or two of arsenite solution at a time.

To determine the reducing action of the arsenite under as nearly as possible the same conditions, add 5 cc. of permanganate from a burette to the hot solution that has just been titrated, and again titrate with arsenite solution until the permanganate is all decolorized. In this way the value of 1 cc. of arsenite solution in cc. of permanganate is determined, and the exact volume of permanganate required to react with the manganese in the analyzed sample can be computed.

If ferric chloride solution was added, then an equally large volume of it should be diluted with hot water, treated with zinc oxide suspension and titrated with permanganate until a pink color is obtained. The volume of permanganate used here should be deducted from that used in the main experiment.

Computation.—Let s represent the weight of sample, a_1, the number of cc. of permanganate used in the main titration, b_1, the number of cc. of arsenite solution used in the main titration, a_2 the number of cc. of permanganate added afterward, b_2 the number of cc. of arsenite required to react with this last permanganate, c the number of cc. of permanganate required by the ferric chloride solution if any were used, and T the value of 1 cc. of permanganate solution in terms of metallic manganese. Then:

$$\frac{[a_1 - b_1 \cdot \frac{a_2}{b_2} - c] \times T \times 100}{s} = \text{per cent. } Mn$$

Test Analyses.—The method has been tested by taking an accurately measured volume of permanganate solution,[1] reducing

[1] *cf.* Wolff, Stahl u. Eisen, **11**, 380; de Koninck, Bull. soc. chim. Belgique, **18**, 56.

it by evaporation with hydrochloric acid, and then titrating with the addition of ferric chloride solution in exactly the same way as in any analysis. The results show that the reaction takes place strictly in accordance with the equation given when the above-described method is used.

TABLE 87.—RESULTS OF MANGANESE DETERMINATIONS IN SAMPLES RICH IN MANGANESE

Nature of sample	Gravimetric method, per cent. Mn	Volumetric method, per cent. Mn
Spiegel	7.84	7.95
	7.81	7.98
Ferromanganese	58.8	59.0
	58.9	58.9
Ferromanganese	82.1	82.0
	81.9	81.9
Metallic manganese[1]	99.1	99.0
	99.1	99.0

TABLE 88.—RESULTS OF MANGANESE DETERMINATIONS IN IRON AND STEEL

Nature of sample	Manganese content		Chromium content determined as on p. 292.
	Gravimetric	Volumetric	
Very mild steel	0.04	0.08	None
Mild steel	0.19	0.22	Trace, <0.01
Steel with 2.5 % Ni	0.28	0.44	0.10
Ordinary steel	0.29	0.39	0.02
Boiler plate	0.44	0.49	0.02
Ordinary steel	0.44	0.52	0.02
Ordinary steel	0.69	0.74	0.01
Tire steel	0.82	0.90	0.03
File steel	0.97	1.10	0.19
File steel	0.98	1.02	Trace, <0.01

[1] The manganese content obtained by deducting all the known impurities was 99.1 per cent. The impurities were 0.40 per cent. Fe, 0.26 per cent. Si 0.06 per cent. Ni, 0.02 per cent. Cu, 0.06 per cent. Al, 0.03 per cent. Pb 0.05 per cent. C, 0.01 per cent. S, 0.008 per cent. P.

Purity of the Zinc Oxide.—Each new lot of zinc oxide should be tested to see if it is sufficiently pure. Dilute 10 cc. of ferric chloride solution with hot water to a volume of about 600 cc., add 4 g. of zinc oxide which has been rubbed into a paste with water, and titrate with permanganate. Repeat the experiment with 10 cc. of ferric chloride solution, 15 cc. of hydrochloric acid (sp. gr. 1.12) and 10 g. of zinc oxide. If the zinc oxide is pure the permanganate consumption will not be greater in the second case than in the first.

Accuracy of Results Obtained by the Modified Volhard Method

The manganese content of a solution containing manganous salt and ferric chloride may be determined within a fraction of a milligram. Too high values are often obtained when the solutions contain substances other than manganous salt which can react with permanganate.

Such substances are chromium, cobalt and vanadium. In the analysis of most kinds of ordinary steel these elements are present only to an inappreciable extent.

Repeated determinations of chromium in ordinary grades of iron and steel to which no chromium was intentionally added, have shown that chromium in small amounts is likely to be present and as a result the Volhard method is likely to give too high values. This, together with the difficulty in obtaining the correct end-point, make the method less suitable for the determination of quantities of manganese less than 1 per cent. than either of the other volumetric methods to be described.

Usually it is possible to obtain duplicate determinations that agree within the following limits:

Manganese Content	Permissible Deviation
1 to 2 per cent.	0.04 per cent.
2 to 10 per cent.	0.06 per cent.
10 upwards	0.1 per cent.

It is difficult to get good results by this method in the analysis of nickel steels. This is partly because the yellowish-green color of nickel solution and the violet of permanganate are

complimentary colors and at the right concentration give a colorless solution. The chief trouble, however, is due to the small quantity of cobalt which is usually present. Cobaltous salts are oxidized by permanganate with the formation of insoluble cobaltic oxide.

(b) Ford-Williams Method

The method depending upon the precipitation of manganese dioxide by the addition of potassium chlorate in nitric acid solution is the best known of those which separate iron and manganese by the precipitation of the latter. In England and in the United States the process is usually attributed to Williams[1] or to Ford[2] and Williams but in Germany it is credited to Hampe[3] or to Beilstein and Jawein. When potassium chlorate is added to a solution containing manganese ions in the presence of strong nitric acid, the following reaction takes place:

$$Mn^{++} + 2ClO_3^- = MnO_2 + 2\,ClO_2$$

The manganese dioxide is obtained as a precipitate and the chlorine dioxide is boiled off as a gas. The precipitate may be dissolved in a measured volume of acid ferrous sulfate solution or hot oxalic acid solution:

$$MnO_2 + 2Fe^{++} + 4H^+ = Mn^{++} + 2Fe^{+++} + 2H_2O$$
$$MnO_2 + 4H^+ + C_2O_4^{--} = Mn^{++} + 2CO_2 + 2H_2O$$

and the excess of reducing agent determined by titration with permanganate.

Procedure.—Weigh out from 2 to 3 g. of steel into a 600 cc. Erlenmeyer flask and dissolve in 60 cc. of nitric acid (sp. gr. 1.2). To prevent loss by spattering, place a small funnel in the neck of the flask. Evaporate the solution to a volume of about 50 cc., add 50 cc. of concentrated nitric acid (sp. gr. 1.42) and 3 g. of potassium chlorate. Boil the solution for 15 min., remove the flask from the source of heat, add 50 cc. more of concentrated nitric acid, 3 g. more of potassium chlorate, and

[1] Trans. Inst. Mining Engineers, **10**, 100.
[2] *Ibid.*, **9**, 397.
[3] Chem. Ztg., **7**, 73.

again boil for 15 min. Do not, in any case, add the potassium chlorate to the nitric acid solution while it is boiling, or an explosion may result. Cool the solution quickly, by placing the flask in cold water, and filter the precipitated manganese dioxide on asbestos. A satisfactory filter is obtained by placing a little glass wool in an ordinary funnel and pouring on it a little suspended asbestos fibers, such as are used for Gooch crucibles. Wash the precipitate with concentrated nitric acid[1] till free from iron and with water till free from acid. Transfer the asbestos pad and precipitate to the original flask, cover with 50 cc. of standard ferrous sulfate solution[2] and dilute with water to a volume of 200 cc. Shake the contents of the flask with small pieces of glass stirring rod to break up the precipitate, until the manganese is all dissolved, and then titrate with 0.03 normal permanganate. The ferrous sulfate solution must be standardized against the permanganate solution the same day the analysis is made. Measure out 50 cc. of the solution, dilute to 200 cc. and titrate with permanganate.

The permanganate solution may be standardized against sodium oxalate or against sodium thiosulfate as described on pp. 205 to 207. If the permanganate solution is standardized against sodium oxalate, the value of 1 cc. in terms of sodium oxalate multiplied by the factor $\frac{Mn}{Na_2C_2O_4} = \frac{54.93}{134.0} = 0.4099$ will give the value of 1 cc. permanganate in terms of metallic manganese.

Computation.—In this method of titration, two molecules of permanganate are equivalent to 5 atoms of manganese, whereas in the Volhard method 2 molecules of permanganate are equivalent to 3 atoms of manganese. Hence, the manganese equivalent of 1 cc. of permanganate is $\frac{5}{3}$ times as large as its value in the Volhard method. This is because in the Volhard titration the manganese of the permanganate is reduced from the valence of seven to the valence of four, while in the Williams method it is reduced to the valence of two.

Let s represent the weight of sample taken for analysis, n_1 the number of cc. of permanganate used in titrating the excess of

[1] The nitric acid must be free from nitrous fumes as nitrous acid reduces manganese dioxide and makes it soluble in nitric acid.

[2] 10 g., $FeSO_4.7H_2O$, 900 cc. water, 100 cc. conc. H_2SO_4.

ferrous sulfate solution, n_2 the number of cc. of permanganate equivalent to the total quantity of ferrous sulfate solution used, and T the value of 1 cc. permanganate solution in terms of metallic manganese. Then

$$\frac{(n_2 - n_1)\ T \times 100}{s} = \text{per cent. Mn.}$$

Accuracy of the Method.—The precipitate formed by treatment with potassium chlorate is assumed to contain all the manganese in the quadrivalent condition. This is probably not strictly true.[1] Moreover, if the conditions are not right, often some of the manganese is not precipitated.[2] If the manganese dioxide precipitate stands for some time it becomes less readily soluble in the ferrous sulfate solution. In spite of these objections, however, the results obtained are usually satisfactory and the method is more suitable than the Volhard method for steels containing less than 0.6 per cent. manganese.

(c) The Sodium Bismuthate Method

Among the reagents used in the analysis of iron and steel for the quantitative conversion of manganous ions in nitric acid solution into permanganic acid are lead peroxide and red lead, ammonium persulfate in the presence of silver nitrate as catalyzer, bismuth tetroxide and sodium bismuthate. Of these reagents, all except the last two are used in a hot solution. Permanganate solutions are readily decomposed on heating, particularly in the presence of unoxidized manganous ions, and for this reason a reagent which requires heat is, on the whole, less suitable than one which is effective in the cold.

Schneider[3] originally proposed the use of bismuth tetroxide and titrated the permanganate formed with hydrogen peroxide. Campredon,[4] Mignot[5] and Jaboulay[6] adopted bismuth tetroxide

[1] Stone, Trans. Inst. Min. Engineers, **11,** 323; **12,** 295, 514. Mackintosh, *Ibid.*, **12,** 79, **13,** 39.

[2] Barreswil, Compt. rend., **44,** 677; see also Moore, Chem. News, **64,** 66; Hampe, Chem. Ztg., **1883,** 1109.

[3] Ding. poly. J., **269,** 224.

[4] Rev. chim. ind., **9,** 306 (1898).

[5] Ann. chim. anal., **5,** 172 (1900).

[6] Rev. gén. chim., **6,** 119 (1903).

as reagent but Reddrop and Ramage[1] used sodium bismuthate because it can be obtained more readily free from chloride, which interferes with the formation of permanganate. Ibbotson and Brearley[2] replaced the hydrogen peroxide by ferrous ammonium sulphate. A. A. Blair[3] called attention to the process and characterized it as more accurate than any other method, volumetric or gravimetric, for the determination of manganese in quantities up to about 2 per cent. Blum has recently studied the method most carefully and has shown that it can be used even with materials rich in manganese.[4]

When sodium bismuthate is added to a cold solution of manganous salt, containing considerable free nitric acid and no chloride or reducing substance, the colorless manganous cations are converted into purple permanganate anions:

$$5BiO_3^- + 2Mn^{++} + 14H^+ = 2MnO_4^- + 5Bi^{+++} + 7H_2O$$

The excess of the reagent is insoluble and can be removed by filtration through asbestos. The permanganate ions on being treated with an excess of ferrous ions are changed back to manganous cations:

$$MnO_4^- + 5Fe^{++} + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$$

and the excess of ferrous ions can be titrated with standardized potassium permanganate solution.

Reagents Required

1. *Sodium Bismuthate.*—The product sold under this name is of more or less indefinite composition but corresponds fairly closely to the formula $NaBiO_3$. It may be prepared by heating 20 parts of caustic soda nearly to redness in an iron or nickel crucible, adding, in small quantities from time to time, 10 parts of dry, basic bismuth nitrate, followed by 2 parts of sodium peroxide and finally pouring the brownish-yellow fused mass on an iron plate to cool. When cold, wash the mass

[1] J. Chem. Soc., **67**, 268 (1895).
[2] Chem. News, **84**, 247 (1901).
[3] J. Am. Chem. Soc., **26**, 793 (1904).
[4] *Ibid.*, **34**, 1382 (1912).

4 or 5 times by decantation with water, collect on an asbestos filter and dry at 110°. The compound is somewhat unstable and if kept over 6 months it should be tested to see if its oxidizing power is still sufficient. Dark brown samples appear to be just as efficient as others which are yellow.

2. *Nitric Acid.*—For dissolving the sample, use nitric acid (sp. gr. 1.13) which may be prepared by diluting concentrated nitric acid (sp. gr. 1.42) with three volumes of water. This acid, as it contains 25 per cent. of the concentrated acid by volume, will be called the 25 per cent. acid (it contains about 22.5 per cent. of anhydrous HNO_3 by weight). For diluting the solution, use 3 per cent. nitric acid, prepared by diluting 30 cc. of concentrated nitric acid to a liter. All the nitric acid used in this analysis must be free from nitrous acid. Since Reynolds and Taylor[1] have shown that nitric acid as weak as 10 per cent. is decomposed by light and that recombination takes place in the dark, the bottles of concentrated nitric acid and of 25 per cent. acid should be preserved in the dark. Nitrous acid reacts with permanganate precipitating manganese dioxide, so that if nitrous acid is present in the solution treated with bismuthate, some of the manganese may be left on the filter. Moreover, if a ferrous salt is titrated with permanganate in the presence of nitric acid containing some nitrous acid, an excessive amount of permanganate will be required.

3. *Potassium Permanganate Solutions.*—For steels containing less than 1 per cent. of manganese 0.03*N* permanganate (0.95 g. $KMnO_4$ per liter) is suitable; for higher manganese content a 0.1*N* permanganate (3.16 g. $KMnO_4$ per liter) should be used. The addition of 10 g. caustic potash per liter lessens the tendency of the permanganate solution to change on standing.[2] The conditions recommended by McBride[3] for standardizing tenth-normal permanganate against sodium oxalate are briefly as follows: Volume, 250 cc.; acidity, 2 per cent. concentrated sulfuric acid by volume; initial temperature, 80° to 90°; slow addition of permanganate especially at the beginning and end; final temperature not less than 60°; end point correction with

[1] J. Chem. Soc., **101,** 131 (1912).
[2] Blum, J. Am. Chem. Soc., **34,** 1379.
[3] J. Am. Chem. Soc., **34,** 415 (1912).

a blank containing a known amount of permanganate. For standardizing the 0.3*N* solution not more than 0.075 to 0.1 g. of sodium oxalate should be taken.

4. *Ferrous Sulfate or Ferrous Ammonium Sulfate Solutions.*—There is little choice between these substances as regards the stability of their solutions. For use with 0.03*N* permanganate weigh out 12.4 g. of ferrous ammonium sulfate, or 8.8 g. of ferrous sulfate crystals, add 50 cc. of concentrated sulfuric acid and dilute to 1 liter. For use with 0.1*N* permanganate, take 39.2 g. of ferrous ammonium sulfate or 27.8 of ferrous sulfate and the same volumes of sulfuric acid and water as before. No appreciable change takes place in the ferrous content of these solutions during a period of a few hours. The 0.1*N* ferrous solutions lose about 1 per cent. in reducing power in 5 days. The solutions should be titrated against the permanganate, therefore, on the same day that the analyses are made.

To determine the reducing power of the ferrous solutions, take 50 cc. of 25 per cent. nitric acid and add a little sodium bismuthate. Shake and allow to stand a few minutes. Dilute with 50 cc. of 3 per cent. nitric acid, filter through an asbestos filter and wash with 100 cc. of 3 per cent. nitric acid. To the clear filtrate add 50 cc. of ferrous sulphate, or the amount to be used in the analysis, and titrate at once with permanganate to the first visible pink.

The treatment with bismuthate is not absolutely necessary but it affords a convenient way for testing the efficacy of the filter.

Procedure for Steels.—Weigh about 1 g. of the sample into a 200 cc. Erlenmeyer flask and dissolve in 50 cc. of the 25 per cent. nitric acid. When the steel has all dissolved, cool somewhat and add sodium bismuthate in small portions until a permanganate color persists on boiling, or becomes decomposed into manganese dioxide. Usually 0.5 g. of bismuthate is sufficient and can be measured sufficiently accurately by means of a small horn spoon. This preliminary oxidation with the bismuthate is essential. It serves to oxidize all substances in the solution which may react with sodium bismuthate or with permanganate. To reduce the manganese again to the bivalent condition, without affecting the other interfering substances

which have been oxidized by the bismuthate, add a little sulfurous acid, hydrogen peroxide or pure ferrous sulphate crystals. Heat for 2 min. to remove oxides of nitrogen and then cool to about 15°. To the cold solution add an excess of bismuthate (usually 0.5 to 1 g.) and shake well for half a minute. Wash down the sides of the flask with 50 cc. of 3 per cent. nitric acid, filter through asbestos and wash with 50 to 100 cc. of the same acid, making sure that the last washings are colorless. A suitable asbestos filter may be prepared by tamping down a wad of glass wool into an ordinary funnel and pouring over it a little of the asbestos-fiber-suspension such as is used for Gooch crucibles. Asbestos fibers on a platinum cone, or in a Gooch crucible, or the asbestos filter used for carbon determinations (*cf.* p. 166), may be used instead. To the clear filtrate, add 50 cc. of standard ferrous solution from a pipette and at once titrate to a pink end-point with permanganate.

Procedure for Cast Iron.—Dissolve 1 g. in 25 cc. of 25 per cent. nitric acid in a small beaker. When all action has ceased, filter into a 200 cc. Erlenmeyer flask. Wash the filter with 30 cc. of the 25 per cent. nitric acid and proceed as with steels.

The removal of the carbonaceous residue is essential as otherwise it is almost impossible to convert all the manganese to permanganate. If it is desired to test an insoluble residue for manganese, volatilize the silica by treatment with sulfuric and hydrofluoric acids, fuse the residue with a little potassium pyrosulfate (potassium acid sulfate heated until it begins to fume), take up the fusion in 25 per cent. nitric acid, and then treat with sodium bismuthate.

In the analysis of white irons, it may be necessary to treat the solution several times with sodium bismuthate in order to destroy all the iron carbide in the preliminary treatment. Otherwise, the carbide will prevent the quantitative conversion of the manganese to permanganate.

Procedure for Ferro-manganese.—Treat 1 g. with 25 per cent. nitric acid exactly as in the analysis of steel. Dilute the solution to 500 cc. in a calibrated flask and take an aliquot part corresponding to from 0.01 to 0.02 g. of manganese. Add 12 to 15 cc. of concentrated nitric acid (sp. gr. 1.42), dilute to 50 or 60 cc., and treat with sodium bismuthate in the usual way.

Procedure for Ferro-silicon.—Treat 1 g. with sulfuric and hydrofluoric acids and heat until thick fumes of sulfuric acid are evolved. Cool and dissolve in 25 cc. of 25 per cent. nitric acid. Transfer to a 200 cc. flask, rinse the dish or crucible with 25 cc. more of the same acid, and proceed as usual.

Procedure for Special Steels.—Steels containing chromium offer no special difficulties. In a hot solution the chromium is oxidized by the bismuthate to chromic acid and the manganese is left in the form of manganese dioxide; both are reduced by the sulfurous acid, or other reducing agent, and in cold solutions the oxidation of the chromium by sodium bismuthate takes place so slowly that the results of the manganese determination are not affected if there is no delay in filtration. Steels containing tungsten are sometimes troublesome on account of the necessity of removing the tungstic acid. Steels that decompose readily with nitric acid yield, after filtering off the tungstic acid, solutions which may be treated like those obtained with cast iron. If it is necessary to use hydrochloric acid for dissolving the sample, it should be removed by repeated evaporation with nitric acid.

Computation.—In this method of analysis it is obvious that 1 molecule of potassium permanganate is equivalent to 1 atom of manganese. Hence the manganese equivalent of 1 cc. permanganate is two-thirds as large as in the Volhard method and two-fifths as large as in the Williams method.

$$1 \text{ cc. } 0.03N \text{ } KMnO_4 \text{ solution} = \frac{0.03 \times Mn}{5000} = 0.0003296 \text{ g. Mn}$$

$$1 \text{ cc. } 0.1N \text{ } KMnO_4 \text{ solution} = \frac{0.01 \times Mn}{5000} = 0.001099 \text{ g. Mn}$$

If s represents the weight of sample, n_1 the number of cc. of permanganate used in titrating the excess of ferrous solution, n_2 the number of cc. of permanganate equivalent to the entire quantity of ferrous salt added, and T the value of 1 cc. permanganate in terms of Mn, then

$$\frac{(n_2 - n_1)\ T \times 100}{s} = \text{per cent. Mn.}$$

Accuracy of the Method.—When the conditions are right, the bismuthate process is certainly as accurate as any known method

for determining manganese in solutions containing less than 0.05 g. of the element. In the analysis of samples rich in manganese, satisfactory results are obtained by using an aliquot part of the original solution. Blum[1] tested the method in four ways; with a manganese sulphate solution of known manganese content, by reducing a measured volume of permanganate and oxidizing it again with sodium bismuthate, by analyzing potassium permanganate crystals and by analyzing a standard manganese ore. Concordant results within one part in five hundred were obtained. The oxidation of the manganese to permanganate is quantitative in well-agitated solutions at temperatures below 25° and the acidity of the solution, when the bismuthate is added, may vary between 20 and 40 per cent. in a volume of 50 to 150 cc. The preliminary treatment with sodium bismuthate should never be omitted and any difficultly soluble residue containing oxidizable material must be removed by filtration, as mentioned in the above directions.

[1] Loc. cit.

CHAPTER IV

PHOSPHORUS

Phosphorus, in varying quantities, is found in all kinds of iron and steel as well as in the various alloys used in steel making. Sometimes for special purposes, iron-phosphorus alloys are prepared containing as much as 25 per cent. of phosphorus. In materials low in phosphorus it is present in solid solution with the iron but in materials rich in phosphorus (over 1.7 per cent. P) it is also present in the form of free phosphide of iron.

As phosphorus shows a marked tendency toward segregation, it is necessary to exercise particular pains in selecting the sample for analysis.

1. DETERMINATION OF PHOSPHORUS IN MATERIALS SOLUBLE IN NITRIC ACID

(a) By Weighing Ammonium Phosphomolybdate (Finkener)

Principle.—The first problem involved in the accurate determination of the phosphorus is the conversion of all the phosphorus into phosphoric acid.

When steel is dissolved in nitric acid (sp. gr. 1.18), a part of the phosphorus is converted into phosphoric acid but the remainder is left in solution in the form of less highly oxidized acids, such as phosphorous acid. In order that this phosphorus may be made to react with the ammonium molybdate, it is necessary to convert it into phosphoric acid by means of a more energetic oxidizing agent or by evaporating to dryness and baking the residue.

With regard to the completeness of the precipitation of phosphoric acid by means of ammonium molybdate solution, Hundeshagen[1] has emphasized the following facts:

1. Free hydrochloric and sulfuric acids, or too concentrated nitric acid, prevent the complete precipitation of the phosphoric acid.

[1] Z. anal. Chem., **28**, 141 (1889).

2. Small quantities of free nitric acid and salts of monobasic acids (chlorides, bromides) have no harmful effect.

3. Ammonium nitrate has a marked accelerating effect upon the precipitation of ammonium phosphomolybdate.

Raising the temperature also hastens the formation of the precipitate but when the precipitation takes place in the cold, as recommended by Finkener, there is less danger of an excess of molybdic acid being thrown down; this is important in all cases where the precipitate itself is to be weighed or the molybdenum in it determined as a measure of the phosphorus content.

When arsenic, tungsten or vanadium is present, the process which is to be described first cannot be used without modification.

Requisite Solutions.—According to Finkener's directions, prepare 2 liters of ammonium molybdate reagent by dissolving 80 g. of finely powdered ammonium molybdate in a large Erlenmeyer flask with 640 cc. of water and 160 cc. of 20 per cent. ammonia (sp. gr. 0.925). Shake the flask vigorously to hasten the solution. Prepare a mixture of 960 cc. of 30 per cent. nitric acid (sp. gr. 1.18) and 240 cc. of water in a two-liter, glass-stoppered bottle, cool the mixture and slowly add to it the ammonium molybdate solution in small portions, with shaking.

Before using this reagent, it should be allowed to stand a few days in a dark place; at the end of this time a small quantity of yellow precipitate will have formed. Decant off the solution from the precipitate and filter if necessary.

Wash Liquid.—Dissolve 150 g. of ammonium nitrate in water, add 10 cc. of concentrated nitric acid (sp. gr. 1.4) and dilute with water to a volume of 1 liter. Use this solution for washing the ammonium phosphomolybdate precipitate.

Procedure.—Weigh out 4 or 5 g. of iron or steel turnings[1] into a porcelain casserole (about 14 cm. in diameter), cover the latter with a watch-glass, and dissolve the sample by adding 50 to 75 cc. of dilute nitric acid (sp. gr. 1.18) in small portions. Evaporate the solution to dryness and decompose the nitrates by strong ignition; this serves to make sure that all of the phosphorus is oxidized to the quinquevalent condition.

[1] To obtain a good average sample it is not advisable to weigh out too small a sample but better to use a large sample and take an aliquot part for the phosphorus determination.

Take up the residue with hydrochloric acid and remove the silica exactly as described for the determination of silicon by Method 1b (p. 173).[1]

Carefully wash the silica on the filter with hot dilute hydrochloric acid (400 cc. water and 100 cc. conc. HCl) and concentrate the entire filtrate, to remove as much as possible of the free hydrochloric acid, by evaporating to the consistency of sirup. Do not continue the evaporation to the point where salts crystallize out on cooling as this will cause basic salts to be precipitated.

If much phosphorus is present, or if it is desired to determine manganese or nickel in the same sample, dilute the solution up to the mark in a 250 cc. calibrated flask, take an aliquot part sufficient for the phosphorus determination and evaporate it nearly to dryness, as just described.

Cool the concentrated ferric solution, add 50 to 100 cc. of ammonium molybdate solution, according to the presumable phosphorus content, and stir vigorously to promote the formation of the precipitate. Allow it to stand half an hour in the cold and add enough solid ammonium nitrate to make the solution contain 25 per cent. of the solid salt, stirring until all of it has dissolved. If 100 cc. of ammonium molybdate reagent were added and the original solution had a volume of about 10 cc., then 28 g. of ammonium nitrate is the proper quantity. This causes the temperature of the liquid to fall noticeably and the precipitation is made complete. After standing 18 to 24 hr. at the room temperature, decant off the solution above the yellow precipitate of ammonium phosphomolybdate through a well-running filter into an Erlenmeyer flask. When all the supernatant liquid has been poured off, replace the Erlenmeyer flask beneath the filter with a clean flask, transfer the precipitate to the filter and wash a few times with the prescribed acid ammonium nitrate solution. If, during the washing, some of the precipitate runs through, filter this portion of the filtrate again. Continue the washing with the ammonium nitrate solution until a little of the filtrate gives no reaction for iron with potassium ferrocyanide or potassium thiocyanate. Test the main filtrate to see if precipitation was complete, by adding a little more of

[1] The process may be shortened as outlined on p. 200.

the reagent and allowing the solution to stand a few hours before discarding it.

If the ammonium phosphomolybdate precipitate is at all bulky, rinse as much of it as possible, with distilled water from a wash bottle, into a weighed porcelain crucible (45 cc. capacity) and evaporate to dryness on the water bath. Dissolve the residual precipitate that adheres to the sides of the beaker in a little dilute ammonia and wash the filter with this ammoniacal solution, catching it in another porcelain crucible (unweighed). Wash the beaker and the filter with dilute ammonia until free from molybdenum salt. (A test for molybdenum can be made by introducing a little hydrogen sulfide into the ammoniacal washings and acidifying; brown molybdenum sulfide will then form if any molybdenum remains.) Evaporate this ammoniacal solution on the water bath until the odor of ammonia can scarcely be detected. Pour about 5 drops of strong nitric acid (sp. gr. 1.4) upon the dry residue in the weighed crucible, add the contents of the other crucible and wash it out with water. Evaporate to dryness on the water bath again and, when perfectly dry, ignite on the Finkener tower until all the ammonium nitrate has been volatilized. Particular pains must be taken with a bulky precipitate to avoid loss by spattering. It is best, therefore, to place the crucible on a thin clay or nichrome triangle over the three gauzes of the Finkener tower (Fig. 118) and heat until the contents of the crucible are perfectly dry, then remove the lower gauze and finally, when the fumes of ammonium nitrate begin to diminish, the middle gauze. Continue the heating until no more fumes are evolved, then take the crucible in the tongs and gently heat the sides of the crucible with the naked Bunsen flame to make sure that all the ammonium nitrate is decomposed. This heating must not be continued to the point where the precipitate assumes a bluish green or blue tint.

Place the crucible in a desiccator over sulfuric acid and allow it to cool there with a weighed watch-glass upon it. After 20 to 25 min. weigh as quickly as possible with the watch-glass remaining on the crucible. This precaution is necessary inasmuch as the precipitate is hygroscopic. Heat gently again and weigh in the same manner, continuing the treatment until two successive weights do not vary more than 0.5 mg.

In case the ammonium phosphomolybdate precipitate is small in amount, it is unnecessary to attempt to rinse it directly into the weighed crucible. Instead of this, dissolve at once the residual precipitate in the beaker with ammonia, pour the solution through the filter allowing it to run into a weighed crucible (25 to 45 cc. capacity), and wash the filter with dilute ammonia until all the precipitate is removed. Evaporate the solution in the crucible until the odor of ammonia is barely perceptible, but do not evaporate until solid salt separates out. Add a little concentrated nitric acid to precipitate ammonium phosphomolybdate again, evaporate to dryness and heat over the Finkener tower as described above.

Computation.—When the above directions are carefully followed, the weighed precipitate corresponds to the formula $(NH_4)_3PO_4 \cdot 12MoO_3$ and contains 1.64 per cent. P.

If p represents the weight of the precipitate and s that of the original substance then

$$\frac{1.64p}{s} = \text{per cent. P}$$

Remark.—The above directions are too involved to be of use in a busy laboratory when a large number of phosphorus determinations have to be made every day. The following simpler procedure has been found to give satisfactory results and is based upon the directions recommended in 1907 by a Committee on Standard Methods chosen by the American Foundrymen's Association.

(b) Rapid Gravimetric Method

Ammonium Molybdate Solution.—Dissolve 100 g. of pure molybdic-acid-anhydride (MoO_3) by stirring it into a mixture of 150 cc. of concentrated ammonia (sp. gr. 0.90) and 250 cc. of water. When all is dissolved, add 65 cc. of concentrated nitric acid (sp. gr. 1.42). Pour the *cold* solution into a *cold* mixture of 400 cc. concentrated nitric acid and 1100 cc. of water, stirring constantly. Add a few drops of ammonium phosphate solution and allow to stand long enough for a slight precipitate of ammonium phosphomolybdate to settle out. Filter before using. The solution does not keep very well and for this reason the

analysis should always be made with a solution that has not been standing too long.

Procedure.—Dissolve 2 g. of borings in 50 cc. of nitric acid (sp. gr. 1.2) and 10 cc. of hydrochloric acid (sp. gr. 1.2)[1] in a porcelain evaporating dish. Evaporate the solution to dryness and bake the residue at a temperature of approximately 200° until free from acid. This baking serves to oxidize carbonaceous matter and to complete the oxidation of the phosphorus to phosphoric acid. Dissolve the residue by heating it with 25 to 30 cc. of concentrated hydrochloric acid, dilute the solution to about 60 cc. and filter into a 250 cc. Erlenmeyer flask. Evaporate the filtrate to about 25 cc., add 20 cc. of concentrated nitric acid and evaporate till a film begins to form on the surface of the liquid. Add 30 cc. of nitric acid (sp. gr. 1.2) and again evaporate till a film begins to form. Dilute with hot water to a volume of about 150 cc., cool to between 70 and 80°, add 50 cc. of ammonium molybdate solution and shake, or stir vigorously, for a few minutes. Filter through a weighed Gooch crucible and wash the precipitate 3 times with 3 per cent. nitric acid and twice with alcohol. Dry the crucible to constant weight at 105°. Assume that the precipitate contains 1.63 per cent. of phosphorus.

(c) Rapid Volumetric Methods

(α) Reduction of the Molybdenum and Titration with Permanganate

This method was recommended some years ago by a committee of American chemists consisting of W. P. Barba, A. A. Blair, T. M. Drown, C. B. Dudley and P. W. Shimer. It gives accurate results when the prescribed conditions are carefully maintained. It depends upon the precipitation of the phosphorus as ammonium phosphomolybdate under conditions such that the ratio of P : Mo = 1 : 12 is maintained, the solution of the precipitate in dilute ammonia, acidification with sulfuric acid, reduction of the molybdenum by zinc and titration back to the hexavalent condition by means of potassium permanganate.

1. *Ammonium Molybdate.*—Stir 100 g. of pure molybdic acid

[1] If the sample is high in phosphorus it is better to use half the above quantities of sample and of reagents.

anhydride into 400 cc. of cold distilled water and add 80 cc. of strong ammonia (sp. gr. 0.90). When all is dissolved, filter, and add it, with constant stirring, to a cold mixture of 400 cc. strong nitric acid (sp. gr. 1.42) and 600 cc. water. Add 50 mg. of microcosmic salt dissolved in a little water, stir well, and allow it to stand 24 hr. Filter before using.[1]

2. *Dilute Nitric Acid* (sp. gr. 1.13).—This acid, containing approximately 25 per cent. nitric acid by weight as well as 25 per cent. of strong nitric acid by volume, is prepared by diluting concentrated nitric acid (sp. gr. 1.42) with three volumes of water.

3. *Dilute Sulfuric Acid.*—Add 25 cc. of concentrated sulfuric acid (sp. gr. 1.84) to 1 liter of water.

4. *Dilute Ammonia.*—Dilute strong ammonia with 1.5 times its volume of water. The solution should have a sp. gr. of 0.96 and contain 9.9 per cent. NH_3 by weight. Since the acidity of the solution from which the ammonium phosphomolybdate is precipitated determines the completeness of the precipitation, and, to some extent, its composition, it is advisable to test the density of the dilute nitric acid and of the ammonia by means of a Westphal balance or delicate hydrometer. The specific gravities given are assumed to be taken at 15° and referred to water at the same temperature.

5. *Acid Ammonium Sulfate.*—To 1 liter of water add 15 cc. of strong ammonia (sp. gr. 0.90) and 25 cc. of strong sulfuric acid. Stir well.

6. *Strong Permanganate Solution.*—Dissolve 12 to 15 g. of permanganate in 1 liter of water and filter through asbestos. This reagent is used to complete the oxidation of the phosphorus to phosphoric acid and destroy carbonaceous matter from the carbides in steel. This was accomplished in the previous methods by baking the residue obtained after evaporating the acid solution of the sample.

7. *Standard Permanganate Solution.*—Dissolve about 2 g. of potassium permanganate crystals for each liter of solution desired. In order that the solution may keep well, it is best to use the same care in preparing it as described on p. 204.

[1] The final solution obtained by these directions is practically identical with that obtained by the directions given on p. 227.

Any good method of standardizing a permanganate solution is perfectly satisfactory. It is a very common practice, however, to use metallic iron wire for this purpose; such a method will be described and it involves the use of the Jones reductor, which is also recommended for use in the phosphorus determination.

The Jones reductor, Fig. 125, consists of a glass tube *A* about 30 cm. long and with an inside diameter of about 18 mm.; at the bottom of the tube a piece of platinum gauze is placed or some glass beads. Then follows a plug of glass wool and a thin layer of asbestos such as is used for Gooch crucibles. The layer of asbestos on the glass wool should be somewhat less than 1 mm. in thickness. If too little asbestos is used, the zinc will pass through into the flask and cause trouble in the subsequent titration. Too thick a layer, on the other hand, soon becomes clogged and the liquid will pass through too slowly. The tube is finally filled with amalgamated zinc to within 5 cm. of the top and on the zinc is placed a little glass wool to act as a filter.

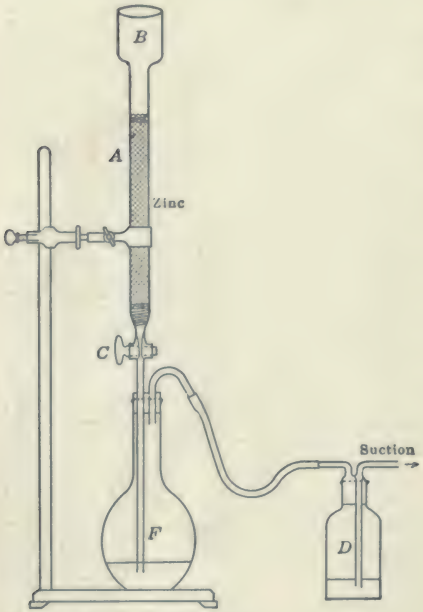


FIG. 125.

The amalgamated zinc is prepared by taking some granulated zinc which will pass through a 20-mesh sieve but not through a 30 mesh, cleaning it with a little hydrochloric acid and adding mercuric chloride solution until hydrogen ceases to be evolved.

Amalgamated zinc is just as efficient as pure zinc with regard to its reducing power upon ferric salts or upon molybdic acid but it does not dissolve readily in dilute sulfuric acid. For this reason the desired reduction can be accomplished by passing the solution through the tube which would be impossible with ordinary

zinc on account of the lively evolution of hydrogen. Before using a Jones reductor after it has been standing for some time it should be washed well with dilute sulfuric acid.

In running a blank, *i.e.*, an experiment with the same quantities of acid and wash water as are to be used in the analysis or standardization,[1] and in all determinations, proceed as follows:

Pour 100 cc. of hot 2.5 per cent. sulfuric acid into the funnel *B* which forms the top of the reduction tube, open the stopcock *C* and apply gentle suction. When only a little dilute acid remains in the funnel, add the solution to be reduced (50 cc. of water, 10 cc. of concentrated sulfuric acid and 5 cc. of dilute ammonia in the case of blanks) and follow it with 250 cc. of hot dilute sulfuric acid (with which the original beaker is washed in several portions) and 100 cc. of water. Air should not be allowed to enter the reductor at any time by letting all the acid or water run out of the funnel, *B*. Before starting any analysis a blank should be run and the volume of permanganate required should not be over 0.2 cc., as a rule. If more is required the blank test should be repeated.

Standardization of Permanganate Solution by Means of Iron Wire

Dissolve about 0.2 g. of standard wire in a 125 cc. Erlenmeyer flask containing 30 cc. of water and 10 cc. of concentrated sulfuric acid. When the iron has all dissolved, boil the solution gently for a few moments in order to expel hydrocarbons.[2] Pass the solution through the reductor, in the manner already described, and titrate slowly with the potassium permanganate solution. Duplicate results in a standardization should agree within 3 parts in one thousand. Greater precision is unnecessary in the analysis of iron or steel for phosphorus.

Analysis of Steel.—Weigh about 2 g. of borings into a 250 cc. Erlenmeyer flask, add 100 cc. of dilute nitric acid (sp. gr. 1.13) and

[1] This is necessary on account of the iron, sulfur, etc., which the zinc contains. An allowance should be made for these impurities whenever zinc is used as a reducing agent.

[2] Many chemists oxidize the carbonaceous matter with strong permanganate, but this is hardly necessary with good iron wire as the error is not more than 2 parts in one thousand and this is far less than the error involved in the determination of small quantities of phosphorus.

insert a small funnel in the neck of the flask. Heat until the sample is all dissolved and the oxides of nitrogen are no longer visible in the flask. Add 10 cc. of the strong permanganate solution, or more if necessary to impart a strong pink color to the solution. Boil until the pink color disappears and manganese dioxide is precipitated. Continue boiling for several minutes, then remove from the source of heat and add a few drops of sulfurous acid, a small crystal of ferrous sulfate, or a solution of 0.5 g. sodium thiosulfate in 10 cc. of water, and repeat the addition of reducing agent at short intervals until all the manganese dioxide has dissolved.[1] Boil 2 min. longer and then cool by placing the flask in cold water or by allowing it to stand in the air until it feels cool to the hand. Add carefully 40 cc. of dilute ammonia and rotate the flask until the precipitated ferric hydroxide all dissolves and a pale yellow solution is obtained. When the solution is at about 35°, add 40 cc. of ammonium molybdate solution, close the flask with a rubber stopper and shake for 5 min. Allow the precipitate to settle for a few minutes and filter. Wash the precipitate several times by decantation and then on the filter with acid ammonium sulfate solution until 2 or 3 cc. of the filtrate give no reaction for molybdenum when tested with yellow ammonium sulfide. It is best to compare the test with a blank made by adding some of the wash liquid itself to a drop of yellow ammonium sulphide solution. When iron is present a black precipitate is obtained while the test solution is still ammoniacal, but with molybdenum the brown sulfide will not form until enough acid ammonium sulfate solution has been added to make the test acid.

Dissolve any of the precipitate remaining in the flask by means of 5 cc. of strong ammonia diluted with 20 cc. of water, and pour this through the filter. Wash out the flask and the filter until the volume of the solution amounts to 60 or 75 cc. Add 10 cc. of concentrated sulfuric acid and pass through the Jones reductor. The solution is preceded and followed by the same quantities of dilute sulfuric acid and water as in running a blank or a standardization. By adding the strong sulfuric acid to the ammoniacal solution, the latter is heated enough so that the molybdenum is

[1] If there is considerable residue at this point the solution must be filtered.

reduced readily by the amalgamated zinc. The solution as it passes through the reductor should be bright green in color. Titrate with the standard permanganate solution, avoiding much shaking, until the permanganate color persists for 1 min. While adding the permanganate, the green color disappears, and the solution becomes brown, pinkish yellow and finally colorless before the end point is reached.

Computation.—The amalgamated zinc reduces the molybdenum from the hexavalent to the trivalent condition. The reaction may be represented by the following equation:

$$2MoO_3 + 3Zn + 6H_2SO_4 = Mo_2(SO_4)_3 + 3ZnSO_4 + 6H_2O$$

There is, however, a slight oxidation by the air in the flask, so that correct results are obtained by assuming a reduction to $Mo_{24}O_{37}$ and subsequent oxidation to MoO_3. We have, therefore,

$$Mo_{24}O_{37} + 35O = 24MoO_3$$

$$1P = 12MoO_3 = 35H$$

$$1 \text{ cc. of N.KMnO}_4 \text{ solution} = \frac{P}{35} = 0.0008857 \text{ g. P}$$

If 1 cc. of $KMnO_4$ solution will oxidize a g. of iron or b g. of pure sodium oxalate, then

$$1 \text{ cc. } KMnO_4 = \frac{P}{35Fe} \times a \text{ or } \frac{2P}{35Na_2C_2O_4} \times b \text{ g. P}$$

From the actual burette readings, the volume of permanganate required for the blank must be deducted in both the analysis and in the standardization.

(β) Ferric Alum Modification

Proceed exactly as in the preceding method up to the point of passing the sulfuric acid solution through the reductor. Instead of passing the reduced solution into an empty flask, place in the flask about 50 cc. of ferric alum solution[1] and make sure that the tube from the reductor passes into the solution. In all

[1] Dissolve 100 g. of $Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, $24H_2O$ in 1 liter of water and 25 cc. of concentrated H_2SO_4 and add 40 cc. of sirupy H_3PO_4. The amount of ferric alum solution used should be sufficient to react with all the reduced molybdenum. Blanks should be run, with the same volume of ferric alum in the flask.

other respects the two methods are identical. There is now no oxidation of the trivalent molybdenum by air in the flask but it is converted back to the hexavalent condition by means of the ferric salt and an equivalent amount of the latter is reduced to ferrous salt. In this case, therefore, the ferrous iron is really titrated by the permanganate but the volume of reagent required corresponds to the amount necessary to convert Mo_2O_3 to MoO_3. The computation is the same as before except that 1P = 36H.

(γ) Alkalimetric Method

This method proposed by Hundeshagen and also by Manby was subsequently modified by J. O. Handy. It depends upon the fact that ammonium phosphomolybdate can be dissolved in a known volume of standard alkali solution and the excess of the latter determined by titration with tenth-normal sodium hydroxide using phenolphthalein as an indicator.

Procedure.—Obtain the precipitate of ammonium phosphomolybdate exactly as in the volumetric methods already described and wash the precipitate with 1 per cent. nitric acid until free from iron and with 1 per cent. potassium nitrate solution till free from acid. Transfer the filter and precipitate back to the Erlenmeyer flask in which the precipitation took place, cover with an excess of tenth-normal sodium hydroxide solution, stir until all the precipitate has dissolved and then titrate with tenth-normal nitric acid using phenolphthalein as indicator.

Computation.—The reaction that represents the solution of ammonium phosphomolybdate in sodium hydroxide is

$$2[(NH_4)_3PO_4.12MoO_3] + 46NaOH = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O.$$

The diammonium sulfate is neutral to phenolphthalein. From the above equation it is evident that 1 atom of phosphorus is equivalent to 23 molecules of sodium hydroxide, or 1 cc. of tenth-normal NaOH = 0.0001348 g. P. If the solutions of sodium hydroxide and of nitric acid are each exactly tenth-normal, and T cc. of the former with t cc. of the latter were used in the analysis of a sample of steel weighing 2 g., then

$$\frac{(T - t) \times 0.01348}{2} = \text{per cent. P}$$

It is well to standardize the sodium hydroxide solution against a known weight of the yellow precipitate containing 1.64 per cent. P. By weighing out exactly 2.70 g. of steel,

$$\frac{T - t}{400} = \text{per cent. P}$$

(d) Weighing the Phosphorus as Magnesium Pyrophosphate

(α) The Acetate Method of A. A. Blair (Modified).—Dissolve 5 g. of borings in 80 cc. of nitric acid (sp. gr. 1.2) and when the reaction begins to slacken add 10 cc. of strong hydrochloric acid. Evaporate to dryness and bake until the nitrates are decomposed in order to oxidize all the phosphorus to phosphoric acid. Cool, add 30 cc. of concentrated hydrochloric acid, heat until the ferric oxide has all dissolved and again evaporate to dryness but without baking the residue. Cool, dissolve in 30 cc. strong hydrochloric acid, dilute and filter off the silica (*cf.* p. 170).

Dilute the filtrate from the silica to about 400 cc. and add ammonia until a slight permanent precipitate of ferric hydroxide is formed. Add 200 cc. of a saturated aqueous solution of sulfur dioxide and slowly heat to boiling. The precipitate soon dissolves and the liquid assumes a dark reddish-brown color, which, on further heating, becomes light green or nearly colorless. As soon as this point is reached, add 10 to 20 cc. of concentrated hydrochloric acid and introduce carbon dioxide gas until the excess of sulfur dioxide is expelled. Cool the solution by placing the beaker in cold water, add 1 or 2 cc. of chlorine or bromine water to oxidize a little of the iron, and ammonia very carefully, with constant stirring, until the greenish precipitate of ferrous-ferric hydroxide dissolves with difficulty. Continue the addition of ammonia, drop by drop, until a distinct brown precipitate is formed which becomes green on stirring. If, before this occurs, the precipitate does not appear decidedly red in color, dissolve it with a drop or two of hydrochloric acid, add a little more chlorine or bromine water and repeat the addition of ammonia until a reddish-brown precipitate is obtained and then the green coloration. Ferric phosphate being white, the forma-

tion of a red precipitate shows that there are more ferric ions present than are required to unite with all the phosphoric acid. Now add enough acetic acid (sp. gr. 1.04), drop by drop, until the green part of the precipitate redissolves leaving a reddish precipitate behind, add about 1 cc. of acetic acid more, heat to boiling and keep at this temperature for 1 min. All the phosphorus is then precipitated as ferric phosphate and some of the iron is precipitated as basic ferric acetate, but the greater part of the iron remains in solution in the ferrous state. Filter through a large filter and wash the precipitate once with hot water. The filtrate is at first clear, but becomes turbid on standing in the air, owing to oxidation of the ferrous ions.

Dissolve the precipitate adhering to the sides of the beaker by warming it with about 15 cc. of hydrochloric acid (1 vol. conc. acid : 1 vol. water) and add 10 cc. of bromine water. If necessary, add a few drops more of concentrated hydrochloric acid to complete the solution of the precipitate. Pour the acid solution through the filter and catch the filtrate in a small beaker. Wash the filter well with hot water and evaporate the solution nearly to dryness to expel the excess of hydrochloric acid. Add a filtered solution of 5 or 10 g. of citric acid dissolved in 10 or 20 cc. of water, also 10 cc. of magnesia mixture[1] and enough ammonia to make the solution faintly alkaline. When perfectly cold, add one-half the liquid's volume of strong ammonia and stir well. After standing 12 hr., filter off the precipitate of magnesium ammonium phosphate and wash it with 2.5 per cent. ammonia containing 2.5 g. of ammonium nitrate in 100 cc. Dissolve the precipitate in hydrochloric acid, evaporate to dryness to remove silica obtained from the reagents and the glass, moisten the residue with a little hydrochloric acid, take up with a little water and filter through a small filter. To the filtrate, which should not be over 20 cc. at the most, add 1 cc. of the 50 per cent. citric acid solution, 2 drops of magnesia mixture and reprecipitate the phosphorus in the same way as before. In this way a precipitate is obtained which yields pure magnesium pyrophosphate upon ignition.

[1] Dissolve 55 g. $MgCl_2.6H_2O$, and 70 g. NH_4Cl in water containing a little hydrochloric acid, add 250 cc. of ammonia (sp. gr. 0.96), and dilute to 1 liter. Filter after the solution has stood several days.

Computation.—If p is the weight of ignited precipitate, and s the weight of sample taken, then

$$\frac{2P}{Mg_2P_2O_7} \cdot \frac{100}{s} = \frac{27.87p}{s} = \text{per cent. P}$$

Remarks.—Blair recommends the use of ammonium bisulfite instead of sulfurous acid for the reduction of the ferric salt. Commercial ammonium bisulfite sometimes contains phosphoric acid so that it seems safer to recommend sulfurous acid itself. Again, Blair suggests that hydrogen sulfide be passed into the solution after the excess of sulfur dioxide has been removed, in order to precipitate any arsenic as the trisulfide. Unless this is done some arsenic is likely to be precipitated with the phosphorus. The filtrate from the hydrogen sulfide precipitation is heated to boiling, the excess of hydrogen sulfide expelled by means of a stream of carbon dioxide, and the solution then partly oxidized as described above.

If the material analyzed contains titanium, a compound containing titanic acid, ferric oxide and phosphoric acid is present in the insoluble residue obtained after evaporating the original solution to dryness. This residue should be filtered off, ignited and treated with sulfuric and hydrofluoric acids to remove the silica. After evaporating off the excess of sulfuric acid, fuse the residue with sodium carbonate and extract the fused mass with water. Acidify the aqueous solution with hydrochloric acid and add it to the main solution.

Another difficulty that is likely to be encountered when titanium is present, is the formation of the above-mentioned insoluble compound when the solution obtained by dissolving the acetate precipitate is being concentrated. To avoid this, the evaporation must be watched carefully and citric acid added as soon as any titanic acid begins to separate.

(β) The Molybdate Method

Dissolve the sample as in the last method and continue the treatment up to the removal of the silica. Evaporate the filtrate from the silica to dryness in a porcelain dish and dissolve the residue in as little nitric acid as possible.

Obtain the precipitate of ammonium phosphomolybdate as described on p. 228 and dissolve the precipitate in as little dilute ammonia as possible. Use, for this purpose, a solution of 25 cc. of ammonia (sp. gr. 0.96), diluted to 100 cc. If the ammoniacal solution thus obtained is not perfectly clear, filter it through a small filter and wash with the same dilute ammonia. Add strong hydrochloric acid until a slight permanent precipitate of ammonium phosphomolybdate is obtained and dissolve this with a little ammonia. If the volume of the solution is now more than about 40 cc. concentrate it by evaporation. Then add magnesia mixture[1] drop by drop as long as a precipitate forms and about 2 cc. in excess. Add 10 to 15 cc. of ammonia (sp. gr. 0.96), stir vigorously and allow the liquid to stand from 4 to 6 hr. Filter through a small filter and wash with 2.5 per cent. ammonia until free from chloride. Ignite carefully and weigh as magnesium pyrophosphate.

The computation is the same as in the previous method.

REMARK.—It has been shown repeatedly by many investigators that the results obtained under favorable conditions by weighing the ammonium phosphomolybdate precipitate, or by titrating it, are fully as accurate as those obtained by weighing the phosphorus as magnesium pyrophosphate, according to either of the last two methods. The ammonium phosphomolybdate precipitate contains such a small percentage of phosphorus that a slight error in weighing it, or in determining the molybdenum content by titration, has but little effect upon the result. On the other hand, in the determination of phosphorus in steel as magnesium pyrophosphate, the weight of the final precipitate is so small and the percentage of phosphorus in it so high that the unavoidable analytical errors such as arise from impure reagents and the action of them upon glass are certain to affect the result.

An error of 0.004 per cent. in the estimated phosphorus content of a sample of steel would correspond to an error of 0.0121 g. of ammonium phosphomolybdate on a 5 g. sample of steel but only to an error of 0.0008 g., if weighed as magnesium pyrophosphate. Such an error is probable in the latter case, but not in the former. If, however, the conditions are not right for a normal precipitation of ammonium phosphomolybdate, an excess of

[1] *cf.* p. 236.

molybdic acid, such as is likely to be present if the solution is too hot or if it stands too long before filtering, will have no effect upon the subsequent determination as magnesium pyrophosphate. For this reason, it is well to have such methods as these last two for checking up the results obtained by the more rapid methods and for use when the precipitate of ammonium phosphomolybdate is abnormally large.

2. DETERMINATION OF PHOSPHORUS IN MATERIALS INSOLUBLE IN NITRIC ACID

(Ferrosilicon, Iron Phosphide, etc., and Alloy Steels)

Materials insoluble in nitric acid are attacked best by ignition with a mixture of sodium carbonate and magnesia as described in the determination of silicon (p. 178). Ignite from 1 to 3 g. of the finely pulverized material with 6 to 8 times as much of the sodium carbonate-magnesia mixture (2 : 1).

After the ignition, dissolve the mass in hydrochloric acid and remove the silica in the usual manner. After volatilizing the silica as silicon tetrafluoride by treatment with sulfuric and hydrofluoric acids, fuse the residue with sodium carbonate, dissolve the product of the fusion in hydrochloric acid and examine the solution for phosphoric acid. Concentrate the filtrate from the silica precipitation (or an aliquot part of it if much phosphorus is present) as described on p. 225 and determine the phosphorus as ammonium phosphomolybdate.

Carry out a blank determination with the reagents used and deduct the weight of ammonium phosphomolybdate thus obtained from that obtained in the regular analysis.

In determining the phosphorus content of ferrotitanium and of metallic titanium, wash thoroughly with cold water the product of the ignition with sodium carbonate and magnesia, filter off the insoluble residue and fuse it with sodium carbonate to obtain any residual phosphorus. Extract this second melt with cold water and add the solution to that previously obtained; the residue will contain all the titanium as sodium titanate.[1] Acidify the aqueous extract with hydrochloric acid, evaporate to dryness in order

[1] The residue is not pure sodium titanate as this is hydrolyzed to form an insoluble acid titanate, *i.e.*, a compound containing a high TiO_2 content.

to remove the silica and then determine the phosphorus in the filtrate by precipitation with ammonium molybdate.

3. DETERMINATION OF PHOSPHORUS IN MATERIALS CONTAINING ARSENIC

(Hydrobromic Acid Method)

Influence of Arsenic upon the Precipitation of Phosphorus.—The statements in the literature concerning the effect of arsenic upon the determination of phosphorus in iron and steel are conflicting. Ledebur states that an arsenic content of less than 0.1 per cent. has no effect upon the determination but cites values which are 20 per cent. too high in the case of ingot iron containing 0.37 per cent. arsenic. On the other hand, Frank and Hinrichsen[1] state that the Finkener method for determining phosphorus gives values ranging up to 0.015 per cent. in excess of the truth when the arsenic content is about 0.05 per cent. Cast iron and ingot iron frequently contain this amount of arsenic so that it would seem advisable to take the effect of arsenic into consideration. To make sure that the precipitate of ammonium phosphomolybdate contains none of the corresponding arsenic compound the best way is to remove the arsenic from the solution. Various methods of accomplishing this have been proposed but the hydrobromic acid method to be described accomplishes this most simply and the use of the method is recommended in all cases where an accurate determination of phosphorus is desired in the possible presence of arsenic.

Principle.—If a solution containing arsenic acid, phosphoric acid and ferric chloride is treated with pure hydrobromic acid (sp. gr. 1.419) and evaporated on the steam bath, then, as Rothe showed, all of the arsenic acid is volatilized, probably as arsenic tribromide, and there is no loss of phosphoric acid. Since ferric bromide does not interfere with the precipitation of ammonium phosphomolybdate it is evident that the determination of the phosphorus can be made in the solution freed from arsenic by the Finkener method, described on p. 224.

Commercial hydrobromic acid almost always contains a little

[1] Stahl u. Eisen, **28**, 295. See also Campbell, J. Anal. and Appl. Chem., **1893**, 2.

phosphoric acid as impurity. If there is only little of it present, the simplest way is to carry out a blank phosphorus determination using the same quantities of reagents as in the analysis proper, and make a deduction from the results obtained in the analysis. If, however, there is much phosphoric acid present in the hydrobromic acid, it must be purified by distilling it.

Procedure.—Dissolve 5 g. of the iron or steel in nitric acid (sp. gr. 1.2), and treat the solution exactly as in the Finkener method. To the hydrochloric acid filtrate from the silica precipitate, or to an aliquot part of it when considerable phosphorus is present, add 10 to 20 cc. of pure hydrobromic acid (sp. gr. 1.419 containing about 48 per cent. HBr by weight) and evaporate to dryness on the steam bath.

The hydrobromic acid should not be added to a very concentrated solution of ferric chloride on account of the danger of loss by spattering.

The residue obtained after evaporation is dark red; dissolve it in a little hydrochloric acid and rinse the solution into a beaker of 150 to 250 cc. capacity. Remove the excess of free acid by evaporation and continue the analysis as in the Finkener method, weighing the phosphorus as ammonium phosphomolybdate.

5. DETERMINATION OF PHOSPHORUS IN MATERIALS CONTAINING TUNGSTEN

Principle.—Hinrichsen[1] has shown that when tungsten is present and the determination of phosphorus is carried out by the Finkener method, the ammonium phosphomolybdate precipitate contains tungsten. He finds that if the precipitate is dissolved in ammonia and the ammoniacal solution treated with magnesia mixture while hot, according to the method of Jörgensen,[2] that the resulting precipitate does not contain tungsten. If the precipitation takes place in the cold, however, tungsten is present in the magnesium ammonium phosphate.

Reagent Required.—Jörgensen recommends that the magnesia mixture be prepared from 50 g. of crystallized magnesium chloride ($MgCl_2.6H_2O$) and 150 g. of ammonium chloride per liter.

Procedure.—Dissolve 5 g. of the sample in nitric acid (sp.

[1] Mitt. kgl. Materialprüfungsamt **28**, 229 (1910).

[2] Z. anal. Chem., **45**, 273 (1906).

gr. 1.20), evaporate the solution to dryness, and decompose the nitrates by ignition. Cool, moisten with concentrated hydrochloric acid, and warm with the addition of more hydrochloric acid until the iron is all in solution. Evaporate to dryness again and render the silica and tungsten insoluble by heating to 135° until no more vapors of hydrochloric acid are evolved. Cool, dissolve in as little strong hydrochloric acid as possible and evaporate off as much of the excess acid as can be accomplished without causing the deposition of solid ferric salt. Allow to stand some time, and then add dilute hydrochloric acid and filter.

Wash the residue with dilute hydrochloric acid until the iron is nearly all removed and finish washing with dilute acid ammonium nitrate solution, such as is used for washing the ammonium phosphomolybdate precipitate (*cf.* p. 224); this serves to prevent tungstic acid from forming a colloidal solution and passing through the filter.

Ignite the residue and volatilize the silica in it by treatment with sulfuric and hydrofluoric acids. Fuse with sodium carbonate, extract the melt with water and treat the hot solution with magnesia mixture as in the main solution. In this way the small amount of phosphoric acid is recovered that is deposited with the silica and tungstic acid.

The filtrate from the silica precipitate contains most of the phosphorus; it may also contain a little colloidal tungstic acid. Evaporate the solution (in a 150 or 250 cc. beaker) as far as possible without separation of solid, and precipitate the phosphoric acid by ammonium molybdate as described on p. 225. Filter and wash with acid ammonium nitrate solution.

Dissolve the precipitate in a very little 2.5 per cent. ammonia, receiving the filtrate in a 150 cc. beaker. Usually it is possible to keep the volume of solution down to 20 cc. Cover the beaker with a watch-glass and heat until the solution begins to boil. Add neutral magnesia mixture, drop by drop, as long as any precipitate forms and 1 or 2 cc. in excess. A flocculent precipitate first forms which soon becomes more compact and crystalline.

Stir the solution frequently as it cools and allow it to stand at least 4 hr. before filtering. Wash the precipitate with 2.5 per cent. ammonia (1 vol. ammonia, sp. gr. 0.96, and 3 vol. water) and ignite it in a weighed crucible.

If there is only a slight precipitate of magnesium ammonium phosphate it is better to dissolve it in nitric acid (sp. gr. 1.2) and precipitate again with molybdate solution, adding enough solid ammonium nitrate so that the solution contains 25 per cent. of it. Weigh this precipitate as described on p. 227.

6. DETERMINATION OF PHOSPHORUS IN MATERIALS CONTAINING VANADIUM

(*Vanadium Steel and Ferrovanadium*)

Principle.—In precipitating phosphoric acid in the presence of vanadic acid, the ammonium phosphomolybdate precipitate is not a pure yellow but has an orange-red shade owing to presence of vanadium. It is not possible to remove the vanadium by the method which is applicable when tungsten is present for the vanadium follows the phosphorus in every precipitation. On the other hand, the vanadium may be precipitated quantitatively from the ammoniacal solution of the yellow precipitate by the addition of ammonium chloride. The phosphorus and molybdenum remain in solution.

After the removal of the ammonium vanadate, the phosphoric acid may be determined in the usual manner.

Procedure.—Dissolve from 5 to 10 g. of the sample in nitric acid (sp. gr. 1.2) and remove the silicon as described on p. 200. In the filtrate from the silica, precipitate the phosphorus according to p. 224 and filter off the orange tinted precipitate. Wash thoroughly with acid ammonium nitrate solution, dissolve the precipitate in ammonia, receiving the solution in a 150 cc. beaker, and concentrate the solution to about 20 cc.

During the evaporation of the solution, add a drop of ammonia from time to time; if the solution turns yellow the ammonia should make it colorless again.[1] To the cold, slightly ammoniacal solution add 5 or 6 g. of solid ammonium chloride and stir vigorously so that the solution quickly becomes saturated with

[1] If, besides the vanadium, tungsten is also present, it must be removed with the silica, according to p. 242. Otherwise some of the tungstic acid will remain in the solution and cause difficulty. The presence of tungsten trioxide in the phosphomolybdate precipitate is shown by the fact that the ammoniacal solution of the precipitate is not colorless but yellowish green. From such a solution the vanadium cannot be precipitated satisfactorily by means of ammonium chloride.

the salt. If the quantity of vanadium present is not too small, the solution will become turbid as the ammonium chloride dissolves and a fine, flocculent precipitate of ammonium metavanadate will separate out; the precipitation is complete after about 6 hr.

Filter off the precipitate and wash it with a saturated solution of ammonium chloride (250 g. to the liter) until a little of the filtrate gives no test for molybdenum.

Slightly acidify the filtrate with dilute nitric acid and add a little more ammonium molybdate. Owing to the large amount of ammonium chloride present, the ammonium phosphomolybdate is now precipitated with an excess of molybdic acid in a finely pulverulent form. Dissolve the precipitate in 2.5 per cent. ammonia and precipitate the phosphorus as magnesium ammonium phosphate by the method of Jörgensen (*cf.* p. 242) weighing it as magnesium pyrophosphate.

TEST ANALYSES

1. COMPARATIVE RESULTS OBTAINED BY WEIGHING THE PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE AND AS MAGNESIUM PYROPHOSPHATE

Test 1.—In the analysis of a 4-g. sample of wrought iron the Finkener method gave 0.108 per cent. P and weighing as magnesium pyrophosphate gave 0.107 per cent. P.

Test 2.—Duplicate determinations by weighing the molybdate precipitate from a 5-g. sample of ingot iron low in phosphorus gave 0.0054 and 0.0055 per cent. P. So little phosphorus was present that no attempt was made to weigh it as magnesium pyrophosphate.

Test 3.—In the analysis of ferrophosphorus, a half-gram sample was decomposed by ignition with Eschka mixture. Duplicate determinations gave 24.84 and 24.89 per cent. P by weighing the molybdate precipitate and 24.85 per cent. P by weighing as magnesium pyrophosphate.

2. DETERMINATION OF PHOSPHORUS IN DIFFERENT MATERIALS

Test 4.—In the analysis of ferrosilicon with 78 per cent. Si, decomposition of a 1-g. sample with Eschka mixture and weighing the molybdenum precipitate gave 0.030 and 0.032 per cent. P.

Test 5.—Silicomanganese, decomposed by Eschka mixture, using a 0.5-g. sample and weighing the molybdate precipitate, showed 0.295 and 0.291 per cent. P.

Test 6.—Metallic titanium, decomposed with Eschka mixture and weighing the molybdate precipitate, gave 0.080 per cent. P with a 1-g. sample and 0.087 with a 2-g. sample.

Test 7.—Tungsten steel, after removal of the tungsten, gave a yellow precipitate corresponding to 0.028 per cent. P and the duplicate analysis checked exactly.

Test 8.—Ferrovanadium showed, by weighing the molybdate precipitate and carrying out the analysis as in the absence of vanadium, 0.342 and 0.341 per cent. P. When the analysis was carried out without regard to the vanadium, the results were 0.39 and 0.40 per cent. P.

3. COMPARATIVE RESULTS OBTAINED BY THE MOLYBDATE PROCESS WITH AND WITHOUT THE USE OF HYDROBROMIC ACID

The ferric chloride solution contained 2.4 g. of iron in 15 cc., the arsenic solution contained 0.045 g. arsenic in 5 cc. The arsenic solution was free from phosphorus but 25 cc. of the hydrobromic acid gave a yellow precipitate weighing 0.0064 and 0.0058 g. in two determinations.

TABLE 90.—(a) WITH AMMONIUM PHOSPHATE SOLUTION

Expt. No.	Cubic centimeters of reagents used				Weight of molybdate precipitate in g.	
	Phosphate solution	Ferric chloride solution	Arsenic acid solution	Hydrobromic acid solution	Without correction	Corrected for phosphorus in the hydrobromic acid
1	20	15	.....	.....	0.1882	.....
2	20	15	.....	25	0.1932	0.1871
3	20	15	5	.....	0.2877	.....
4	20	15	5	.....	0.2929	.....
5	20	15	10	25	0.1919	0.1851
6	20	15	10	25	0.1929	0.1868
7	20	15	5	.....	0.2792[1]	.....

[1] In **Expt. 7,** 25 cc. of fuming hydrochloric acid were added instead of hydrobromic acid. The result shows that this acid does not work as well as the hydrobromic acid.

TABLE 91.—(b) WITH IRON AND STEEL SAMPLES

Sample No.	Nature of the material	Phosphorus determined	
		without	with
		using hydrobromic acid, per cent.	
1	Ingot iron	0.025	0.019
		0.021	0.018
2	Wrought iron	0.148	0.127
		0.142	0.126
3	Cast iron	0.048	0.044
		0.049	0.045
4	Good quality Martin pig iron	0.109	0.076
		0.110	0.078
5	Siemens-Martin steel[1]	0.040	0.028
		0.042	0.029
		0.042	0.029
		0.041	0.028

[1] Each pair of analyses was done by a different analyst. The arsenic content of sample 5 was found to be 0.058 per cent.

ACCURACY OF PHOSPHORUS DETERMINATIONS AND PERMISSIBLE DEVIATIONS

Experience has shown that by precipitating phosphoric acid solutions with ammonium molybdate solution, the precipitates may be weighed with an accuracy of about ± 0.001 g. Since a number of other substances give similar precipitates with molybdic acid, or are carried down with the ammonium phosphomolybdate, it is only possible to obtain accurate results when there are no disturbing factors; suitable methods for overcoming difficulties have been given. Assuming that the error involved in weighing the precipitate is $+0.001$ g., then

with P content of	Permissible Deviation
0 to 0.03 per cent.	± 0.001 per cent.
0.03 to 0.1 per cent.	± 0.002 per cent.
0.1 to 0.2 per cent.	± 0.003 per cent.
0.2 to 1.0 per cent.	± 0.005 per cent.
1.0 to 2.0 per cent.	± 0.01 per cent.
2.0 to 5.0 per cent.	± 0.02 per cent.
5.0 and more	± 0.05 per cent.

CHAPTER V

ARSENIC

Arsenic occurs quite commonly in iron ores and for this reason there is likely to be some arsenic in most samples of iron and steel; von Reis found in some cases as much as 0.08 per cent. arsenic.

Inasmuch as arsenic tends to injure the metal, the knowledge of the arsenic content is of importance in judging the value of a given material. The previous chapter has shown the effect of arsenic on the determination of phosphorus so that a knowledge of the arsenic content is of importance to the chemist in helping him to choose a suitable method for that determination.

Principle.—When iron and steel are dissolved in *nitric acid* the arsenic is converted into arsenic acid. On evaporating to dryness and decomposing the nitrates all the arsenic remains in the residue as arsenate.

From the hydrochloric acid solution of the residue it is possible to distil off arsenic trichloride after reducing the iron to the ferrous state by means of a suitable reducing agent.[1] One of the most satisfactory reducing agents in this case is cuprous chloride. The reduction process can then be represented by the ionic equation

$$Fe^{+++} + Cu^{+} = Fe^{++} + Cu^{++}$$

Accordingly, 56 parts by weight of iron require 99 parts by weight of cuprous chloride.

Procedure.—Dissolve 10 to 12 g. of the iron or steel in a 500 cc. round-bottomed flask by the gradual addition of nitric acid (sp. gr. 1.2), and heating over the Bunsen flame. Evaporate to dryness (*cf.* p. 200) and heat the residue until no more nitrous fumes are evolved. Cool and dissolve the residue in 80 to 100 cc. of concentrated hydrochloric acid, warming very gently and rotat-

[1] Some reducing agents, *e.g.*, stannous chloride and sodium hypophosphite, reduce some of the arsenic to the metallic condition and others, *e.g.*, zinc and iron, reduce it to arsine, AsH_3. Ferrous salts reduce quinquevalent arsenic to the trivalent state.

ing the liquid about in the flask. The liquid must not be heated to boiling as there is a chance of some arsenic being lost thereby.

For each 10 g. of sample, add 18 g. of pure, arsenic-free cuprous chloride to the distilling flask, Fig. 126, pour upon it the hydrochloric acid solution of the sample and wash out the contents of the original flask with hydrochloric acid (sp. gr. 1.12). With the apparatus all in place, heat the contents of the distilling flask to boiling and catch the distillate in a 500–600 cc. beaker. When only about 50 cc. of liquid remain in the flask, stop heating, add 50 cc. of concentrated hydrochloric acid (sp. gr. 1.2) and carefully distil again. These two distillations are sufficient to volatilize all the arsenic as trichloride.

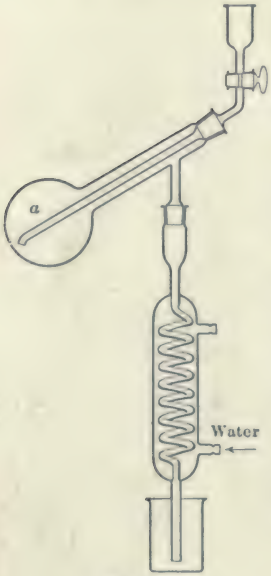


FIG. 126.

Dilute the strongly acid distillate with an equal volume of water, saturate it with hydrogen sulphide and allow the beaker to stand over night under a bell jar.

Filter off the precipitate of arsenic trisulphide through a small, well-running filter and wash with water until the washings are no longer acid. Rinse the precipitate into a small porcelain dish and dissolve the residue on the filter with ammonia, washing thoroughly with water containing ammonia. Concentrate the solution to remove the excess of ammonia and evaporate to dryness after adding concentrated nitric acid. Add a few drops of concentrated nitric acid, to help oxidize the residual sulphur, and evaporate on the steam bath. Dissolve the residue of arsenic acid in a little water, filter through a small filter and concentrate the filtrate, in a small beaker, to a volume of 10 to 20 cc. Add 2 or 3 cc. of magnesia mixture (*cf.* p. 241) half the solution's volume of ammonia water (sp. gr. 0.96) and stir vigorously with a glass rod. The precipitate of magnesium ammonium arsenate soon begins to form. After a short time add a little more magnesia mixture to see if any further precipitation takes place. Finally add alco-

hol corresponding to one-fourth the volume of the liquid and allow the precipitate to stand over night.

Filter off the precipitate through a weighed Gooch or Munroe crucible and wash with 2.5 per cent. ammonia to the disappearance of chlorides. Dry the crucible and its contents at 110° and then heat it in air bath (*cf.* Fig. 123, p. 195) raising the temperature very gradually until a light red heat is obtained. Cool in a desiccator and weigh as magnesium pyroarsenate, $Mg_2As_2O_7$.

Computation.—If s is the weight of the sample and p the weight of the ignited precipitate, then

$$\frac{2As \times p \times 100}{Mg_2As_2O_7 \times s} = \frac{48.27p}{s} \text{ per cent. As}$$

TEST ANALYSES

Experiments with an Arsenic Solution of Known Arsenic Content

Duplicate determination gave the values 0.0338 and 0.0332 g., $Mg_2As_2O_7$ in 10 cc. of the arsenic solution. Experiments were carried out with 10 cc. of the arsenic solution added to 5 g. of Kahlbaum's pure reduced iron (free from arsenic) and the weights of magnesium arsenate obtained were 0.0326 and 0.0328 g.

Experiments with Commercial Iron and Steel

No.	Material tested		Weight taken in g.	Weight of $Mg_2As_2O_7$	Per cent. arsenic
1	Pig iron	*a*	5	0.0034	0.033
		b	5	0.0035	0.034
2	Siemens-Martin steel	*a*	5	0.0024	0.023
		b	5	0.0026	0.025
3	Siemens-Martin steel	*a*	5	0.0066	0.064
		b	5	0.0054	0.052
4	Siemens-Martin steel	*a*	10	0.0128	0.062
		b	10	0.0106	0.051

Accuracy of the Process.—The arsenic content of iron and steel up to 0.3 per cent. As can be determined with an accuracy such that the results are probably correct to within about 0.01 per cent. It is necessary, however, to test all the reagents used by running a blank experiment. This is especially necessary because most hydrochloric acid contains traces of arsenic.

CHAPTER VI

SULFUR

Sulfur, to some extent, occurs in all kinds of iron and steel but the maximum quantity ever found is only a few tenths of 1 per cent. It is always present in the form of sulfides, chiefly of iron and manganese, and such sulfur can be evolved as hydrogen sulfide by treatment with hydrochloric acid. Since sulfur tends toward segregation, care should be taken to procure a good average sample and to use a fairly large amount of material for the analysis.

1. DETERMINATION OF SULFUR IN MATERIALS SOLUBLE IN ACIDS

Outline of Methods Used.—Excellent gravimetric, volumetric and colorimetric methods have been proposed for the determination of sulfur.

The gravimetric methods usually depend upon the oxidation of the sulfur to the sulfate condition and its precipitation as barium sulfate. Morrell,[1] however, weighs the sulfur as cadmium sulfide and Berzelius obtained a precipitate of silver sulfide, dissolved it in nitric acid and weighed the silver as chloride. The problem of determining sulfur in the presence of iron has received a great deal of attention in the literature. Küster and Thiel[2] have shown that enormous errors, sometimes amounting to a loss of one-tenth the entire sulfur content, result from the addition of barium chloride to a boiling solution containing sulfuric acid in the presence of ferric chloride. The loss is due probably in part to the formation of a complex ion containing iron and sulfur which is not completely precipitated and partly to the fact that ferric sulfate, or any complex containing iron and sulfur, loses sulfur upon ignition. These low results, therefore, occur especially when the precipitate is strongly contaminated with iron, as shown by the red stain of

[1] Chem. News, **28**, 229.

[2] Z. anorg. Chem., **22**, 424.

ferric oxide in the crucible after the final ignition. Küster and Thiel found that accurate results could be obtained without the removal of the iron in three ways: (1) by precipitating with ammonia without filtering, heating nearly to boiling, adding the barium chloride slowly, and finally dissolving the ferric hydroxide in dilute hydrochloric acid; (2) by precipitating with barium chloride in a cold solution; (3) by adding the cold ferric chloride and sulfuric acid solution very slowly to a boiling, dilute solution of barium chloride. It is well to remember, however, that the trouble caused by the ferric chloride in the determination of small quantities of sulfur is probably greater in dilute than in concentrated solutions, as Archbutt[1] has shown. On the other hand, barium sulfate has a decided tendency to occlude impurities, and occlusion is likely to be greater in concentrated solutions. In determining large quantities of sulfur, therefore, it is best to work in dilute solutions.

To avoid the harmful effect of ferric chloride upon the sulfur determinations, it has been recommended to reduce the iron to the ferrous condition but this remedy is not usually adopted in iron and steel analysis. A more common expedient is to determine the sulfur in a solution free from iron. This may be accomplished: (1) by expelling the sulfur as hydrogen sulfide and oxidizing the absorbed gas; (2) by removing the ferric chloride by shaking the solution with ether; (3) by precipitating the iron with an excess of ammonia or of sodium carbonate; (4) by treating the iron or steel with acid cupric ammonium chloride, which dissolves the iron and leaves the sulfur in the residue from which it can be obtained by an oxidizing solution and treatment with barium chloride.[2]

The volumetric determination of sulfur in iron and steel is usually based upon the expulsion of the sulfur as hydrogen sulfide and the reaction of this gas with iodine. The details of the method vary considerably, especially with regard to the preliminary absorption of the hydrogen sulfide.

The best-known colorimetric method is that of J. Wiborgh[3]

[1] J. Soc. Chem. Ind., **1890**, 25.

[2] Meinecke, Chem. News, **59**, 107; Boucher, *ibid.*, **74**, 76; Carnot and Goutal, J. Chem. Soc., **72**, II, 520.

[3] Stahl u. Eisen, **6**, 240 (1866).

which depends upon the evolution of the sulfur as hydrogen sulfide, the passage of the gas through a cloth disk which has been dipped in cadmium acetate solution, and the subsequent comparison with a series of similar disks produced by the treatment of steels with known sulfur content. This method is useful in a busy laboratory.[1]

In this book five typical methods will be described, of which only the first two are mentioned in the German text.

(a) Absorption of Hydrogen Sulfide in Bromine and Hydrochloric Acid[2]

Apparatus and Solutions Required

Evolution Apparatus.—Many forms of apparatus have been devised and that shown in Fig. 127 has proved satisfactory.[3]

Kipp Generator for producing pure carbon-dioxide gas.

Bromine and Hydrochloric Acid.—Add about 13 cc. of pure bromine, free from sulfate, to 1 liter of hydrochloric acid (sp. gr. 1.12), and mix thoroughly by vigorous shaking.

Sodium Chloride Solution.—Prepare a 10 per cent. solution of sodium carbonate, free from sulfate, and neutralize with hydrochloric acid.

Procedure.—Weigh out, with an accuracy of 1 cg., about 10 g. of steel into the dry flask of the apparatus shown in Fig. 127. If the material is badly rusted, it is well to add 1 or 2 g. of solid stannous chloride to avoid any oxidation of the sulfur by ferric chloride.

Fasten the top on the apparatus, which has ground glass connections, and replace the air in it by introducing a stream of dry carbon dioxide. While doing this, fill the ten-bulb absorption tube with about 30 cc. of the bromine and hydrochloric acid mixture, using enough to fill all but the last three of the ten bulbs. Connect the tube with the flask and continue passing the stream of carbon dioxide until no more vapors of bromine are visible in the large bulb of the absorption tube. This is usually accomplished in a minute or two.

[1] *cf.* Treadwell-Hall, Analytical Chemistry, Vol. II, p. 354 (3rd edition).

[2] *cf.* Schulte, Stahl u. Eisen, **26,** 985 (1906); Kinder, *ibid.*, **28,** 249 (1908).

[3] Can be supplied by Bleckmann and Burger in Berlin.

Then close the stopcock just above the flask, remove the upper end of funnel which serves for the introduction of gas, and add through the funnel the requisite quantity of hydrochloric acid.

For dissolving 10 g. of iron it is best to use 100 cc. of hydrochloric acid (sp. gr. 1.16 to 1.15).[1] To get this concentration of acid, fill the funnel with 50 cc. of concentrated hydrochloric acid (sp. gr. 1.2), and transfer it to the flask with the aid of carbon dioxide pressure. Then add 50 cc. of hydrochloric acid (sp. gr. 1.12), in the same way, avoiding the introduction of any air into the flask.

If the action of the acid is very violent, cool the flask by placing it in a dish of cold water; if it is slow, heat with a small flame.

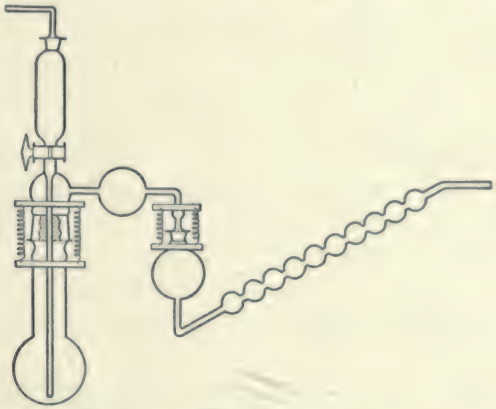


FIG. 127.

While the steel is dissolving, stop passing carbon-dioxide gas through the apparatus, in order to avoid driving off too much of the bromine from the absorption tube. The solution of the sample should take place fast enough so that a good current of gas passes through the mixture of bromine and hydrochloric acid. Gradually increase the heating of the flask until finally the liquid

[1] The use of acid which is more concentrated than this does not give more accurate results. Fuming hydrochloric acid is not suitable because, on heating the flask, too much hydrochloric acid is boiled off and this causes an unnecessary loss of bromine. Moreover, it is more likely to cause the liquid to boil over and sometimes the evolution of the gas is so uneven that bromine vapors are sucked back into the absorption flask, making it necessary to repeat the determination.

in it boils, at which time the entire sample should be dissolved. The dissolving of the steel should not require more than an hour at the most; if more time is required, as in the analysis of some steels containing tungsten or molybdenum, the results are likely to be low.

When all the iron is dissolved, boil for a minute more, then lead a rapid stream of carbon-dioxide gas through the apparatus, remove the flame from beneath the flask and allow the liquid in it to cool.

After 10 or 15 min., take off the absorption tube and stop the current of carbon dioxide. Rinse the contents of the tube into a porcelain dish, add 2 or 3 cc. of pure sodium chloride solution and evaporate to dryness on the water bath in an atmosphere free from sulfuric acid fumes. Moisten the residue[1] with hydrochloric acid, add a little water, warm and filter through a small filter into a beaker of about 100 cc. capacity. Heat the filtrate to boiling and precipitate the sulfuric acid by the slow addition of 5 cc. of barium-chloride solution (100 g. $BaCl_2.2H_2O$ in 500 cc. water). Stir well and allow to stand in a warm place until the barium sulfate has settled out. Then filter through a small ashless filter, taking the precaution to change the beaker under the funnel before getting the precipitate on the filter, and wash first with very dilute hydrochloric acid and finally with hot water till free from chloride.

Ignite the filter and precipitate very gently until the ash is white and finally over the full heat of the Bunsen burner, with the cover of the crucible off. Do not heat over the blast because of the danger of converting barium sulfate into barium oxide.

On account of the possibility of small quantities of sulfuric acid being present in the reagents and the danger of contamination from the atmosphere (due to the use of sulfuric acid or to the burning of illuminating gas in the laboratory) it is always desirable to carry out a blank determination with the same quantities of reagents and the same operations as in the analysis. Moreover, the evaporation, precipitation, filtration, etc., should take place

[1] If the material analyzed contains much carbon, the residue obtained at this stage in the analysis often contains bromine substitution products of hydrocarbons. These color the residue and give it a sharp odor but do not affect the analysis in any way.

at the same time the analysis itself is being made. The weight of barium sulfate obtained in the blank experiment should be deducted from that obtained in the analysis. Such blank experiments are desirable in all determinations of relatively small quantities of substances. When the substance determined is present in large quantities, as in the determination of sulfur in a nearly pure sulfate, the negative errors due to the solvent action of the reagents upon the precipitate may more than compensate the amount obtained from the reagents.

The solution obtained in the distillation flask after the sulfur has been removed as hydrogen sulfide, may be used for other determinations. It is not suitable for the determination of silicon, however, as there is likelihood of small particles of gelatinous silicic acid adhering to the sides of the flask so firmly that they cannot be easily removed. After rendering all the silicic acid insoluble, by the method described on p. 170, the filtrate may be used for the determination of copper, manganese, nickel, chromium or vanadium.

Computation.—The sulfur content of the steel, when s represents the original weight of the metal and p the weight of the precipitate, is

$$\frac{p \times 100}{BaSO_4 \times s} = \frac{13.74p}{s} = \text{per cent. S}$$

(b) Determination of Sulfur by the Ether Method[1]

Necessary Apparatus and Solutions.—The requirements are the same as those specified on p. 184.

Procedure.—Weigh 5 g. of borings into a 500 cc. round-bottomed flask and add 50 cc. of concentrated nitric acid (sp. gr. 1.42). As a rule there is little action in the cold. Heat cautiously at first, holding the flask with a clamp and rotating it over a small flame, and have a dish of cold water ready so that the flask may be placed in it if the reaction should become too violent. After the brown nitrous fumes cease to form, gradually raise the temperature of the acid until it boils. When, at the end of an hour or so, the sample is all dissolved, add 0.25 g. of potassium nitrate dissolved in a little water, evaporate to dryness and heat the residue

[1] *cf.* Krug, Stahl u. Eisen, **25,** 887 (1905).

until no more brown fumes are evolved. After cooling, dissolve the residue by heating it with 50 cc. of concentrated hydrochloric acid (sp. gr. 1.2) and again evaporate to dryness. Redissolve in hydrochloric acid, dilute somewhat and filter off the silicious residue. Evaporate the filtrate until a film of ferric chloride forms and redissolve this film by a few drops of hydrochloric acid. It is now ready for treatment with ether.

After cooling the ferric chloride solution, introduce it into the double separatory funnel shown in Fig. 120, p. 184, and wash out the contents of the dish, or beaker, with hydrochloric acid (sp. gr. 1.1) keeping the total volume of the solution and washings below 60 cc. Add 30 cc. of the mixture of ether and concentrated hydrochloric acid (*cf.* p. 184) and 100 cc. of pure ether. Cool under the water tap and shake thoroughly. The upper, olive-green, ether layer now contains nearly all the iron and the lower, aqueous layer contains all the sulfuric acid. Carefully transfer the lower layer to the other separatory funnel. Add to the ether solution remaining in the upper funnel, a few cc. of the mixture of ether and dilute hydrochloric acid (sp. gr. 1.1). Shake, allow to settle and add the lower layer to the solution in the lower funnel. Introduce 75 cc. of pure ether into this funnel, shake well and finally draw off the lower layer into a porcelain evaporating dish; it contains all the sulfur, very little ferric chloride and some dissolved ether. Evaporate to dryness on the water bath, moisten the residue with a few drops of hydrochloric acid, dilute with a little water and filter into a small beaker. Heat the filtrate to boiling and precipitate the sulfuric acid in the usual way.

Allow the beaker to stand in a warm place for several hours, then filter, wash, ignite and weigh as described under the previous method. It is important to carry out simultaneously with the analysis a blank experiment with the same quantities of reagents.

The computation is the same as for Method *a*.

(c) Bamber Method for Determining Sulfur in Iron or Steel

This method is suitable for the analysis of cast iron or steel and for any iron alloys which are decomposed completely by treatment with nitric acid. It has proved to be a very reliable method.

Procedure.—Dissolve from 3 to 5 g. of the sample in concentrated nitric acid (sp. gr. 1.42). After the iron has dissolved completely, add 2 g. of solid potassium nitrate and evaporate to dryness on the water bath in a platinum dish. Heat the residue to redness using an alcohol flame. After the ignition, add 50 cc. of a 1 per cent. solution of sodium carbonate, boil for a few minutes and filter. Wash the precipitate thoroughly with hot 1 per cent. sodium carbonate solution. Acidify the filtrate with hydrochloric acid and evaporate to dryness. Moisten the residue with 2 cc. of concentrated hydrochloric acid and add 50 cc. of water. Heat to boiling and filter. Dilute the filtrate to 100 cc. and precipitate the filtrate hot with 10 cc. of 2 per cent. barium chloride solution. Ignite and weigh in the usual manner.

(d) Determination of Sulfur in the Presence of Ferric Chloride

In spite of the many objections that have been raised to the direct determination of sulfur in the presence of iron, many chemists still adhere to the old method of dissolving the sample in nitric acid or in aqua regia, evaporating to render the silica insoluble, and precipitating the sulfuric acid from a concentrated solution in the presence of ferric chloride. The method has been used by the Bureau of Standards at Washington in the analysis of standardized specimens of iron and steel and the results have compared favorably with those obtained by other methods.

Procedure.—Treat 5 g. of borings with 50 cc. of concentrated nitric acid (sp. gr. 1.42) in a 400 cc. Erlenmeyer flask. Add about 1 g. of solid sodium carbonate and evaporate to dryness. Bake to decompose nitrates, dissolve the residue in 30 cc. of concentrated hydrochloric acid (sp. gr. 1.2), and again evaporate to dryness for the purpose of making the silica insoluble. Redissolve the residue in 30 cc. of strong hydrochloric acid, evaporate the solution to sirupy consistency, and add 4 cc. of concentrated hydrochloric acid. When all the iron is in solution, add 30 to 40 cc. of hot water, filter off the silicious residue and wash with hot water. Avoid letting the filtrate exceed 100 cc. Heat it to boiling and precipitate with 10 cc. of 10 per cent. barium chloride solution. Allow to stand 24 hr. before filtering.

Fuse the insoluble silicious residue with sodium carbonate and a little potassium nitrate, extract the fusion with hot water, filter, acidify with hydrochloric acid, and evaporate to dryness. Moisten the residue with hydrochloric acid, dilute and filter. Heat to boiling, precipitate hot with 2 cc. of barium chloride solution, and allow to stand over night. The sulfur obtained from this insoluble residue should be added to that obtained from the main solution.

Evaporations should take place in an atmosphere free from vapors containing sulfur and the use of steam baths, electrically heated hot plates, or alcohol burners is to be preferred to gas flames. A careful blank experiment should be carried along at the same time, using the same quantities of reagents and exactly the same operations.

(e) Volumetric Determination of Sulfur with Iodine

The iodometric determination of sulfur in iron alloys is based upon the following reactions:

$$FeS + 2HCl = FeCl_2 + H_2S$$
$$2H_2S + I_2 = 4HI + 2S$$

and, when an excess of iodine is used,

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Usually the gas which escapes on dissolving the sample in hydrochloric acid is not allowed to act directly upon iodine but it is first absorbed by some suitable reagent. Sodium hydroxide or ammoniacal cadmium chloride solution is commonly used but many other absorbents have been proposed. With sodium hydroxide, the resulting solution, which contains the sulfur as sodium sulfide, is diluted to about 500 cc. and acidified with hydrochloric acid. A little potassium iodide added and the hydrogen sulfide is at once titrated with a standard iodine solution, using starch as an indicator. Two objections may be raised to this procedure. First, it is possible that some gas other than hydrogen sulfide may be absorbed by the sodium hydroxide solution and subsequently react with iodine. Second, there is opportunity for a little hydrogen sulfide to escape when the solution is acidified just before the titration.

When an ammoniacal solution of cadmium chloride is used as the absorbent, both of the above objections may be overcome. Cadmium sulfide is precipitated in the liquid absorbent, the precipitate is removed, treated with a measured volume of standard iodine solution, the solution acidified and the excess of iodine titrated slowly with sodium thiosulfate solution.

Apparatus and Solutions.—A simple and suitable evolution apparatus may be constructed as follows: Use a 250 cc. round-bottomed flask as generator. Fit it with a doubly-perforated rubber stopper. Through one hole in the stopper introduce a dropping funnel so that the bottom of the stem reaches nearly to the bottom of the flask and through the other hole introduce a delivery tube, bent twice at right angles, leading into a 250 cc. Erlenmeyer flask, about 1 in. below the stopper. Connect this flask with a second 250 cc. Erlenmeyer flask by means of another tube bent twice at right angles. This tube starts just below the stopper in the first flask and extends nearly to the bottom of the second flask. Connect this flask with a third Erlenmeyer flask in the same way. The first Erlenmeyer serves merely as a guard flask and to remove most of the hydrochloric acid that distils over, whereas the second and third flasks are to contain liquid into which the gas is to be led.

Prepare a solution of sodium thiosulfate by dissolving 5 g. of the crystallized salt, $Na_2S_2O_3 . 5H_2O$, in each liter of freshly boiled and cooled water. Prepare a solution of iodine by dissolving 2.5 g. of iodine in 100 cc. of water containing 5 g. of pure potassium iodide, finally diluting the solution to 1 liter. Both of these solutions are approximately 0.02 normal. Titrate the two solutions against one another and then standardize the sodium thiosulfate against potassium permanganate, p. 206, against pure iodine, p. 287, or against copper, p. 268.

For absorbing the hydrogen sulfide, prepare an ammoniacal solution of cadmium salt by dissolving 120 g. of cadmium chloride in 1500 cc. of water and adding 600 cc. of concentrated ammonia (sp. gr. 0.90). Use 10 cc. of this solution in each of the two absorbing flasks, diluting with 50 cc. of water. If a white precipitate of cadmium hydroxide appears upon dilution, dissolve it by the addition of a little ammonia. Place 25 cc. of water in the first Erlenmeyer flask. This serves to catch most of the hydro-

chloric acid that distils over, but it does not absorb an appreciable amount of sulfur as it is heated nearly to boiling toward the last.

Procedure.—Weigh 5 g. of steel into the generating flask, make sure that all the connections are tight and then add 60 cc. of strong hydrochloric acid (sp. gr. 1.19) through the funnel.[1] As soon as the action of the acid on the metal begins to slacken, gradually apply heat, and finally, when all the metal is dissolved, boil the solution gently until steam condenses in the guard flask. Disconnect the apparatus, first opening the stopper of the dropping funnel so that there will be no back pressure on the removal of the flame.

Filter off the precipitate of cadmium sulfide, which is usually all in the middle flask, and wash the flask and filter twice with water. Transfer the filter and precipitate to a beaker, pour over it 300 cc. of water, add 25 cc. of the standard iodine solution, stir thoroughly and then add 5 cc. of concentrated hydrochloric acid. Dissolve any sulfide precipitate remaining in the flask, or in the glass tubing, by means of a little of this solution, washing it all back into the beaker. Titrate the excess of iodine with the standard sodium thiosulfate solution.

Computation.—If s represents the weight of the steel, n the cc. of thiosulfate used, T the value of 25 cc. of iodine solution in terms of the thiosulfate solution, and N the relation of the thiosulfate to the normal solution, then

$$\text{per cent. } S = \frac{(T - n)N \times 1.6}{s}$$

Applicability of the Methods for Determining Sulfur in Iron and Steel

Comparative tests have repeatedly demonstrated the fact that, when properly carried out, the method last described gives accurate results with most samples of steels. The time required for carrying out the analysis is short and there is no danger of contamination from sulfur in the laboratory atmosphere. If the acid used is too dilute, or if the solution of the steel takes place too slowly, the results are likely to be a little low. Certain samples of cast iron and some steels contain sulfur in a condition such that

[1] If dilute hydrochloric acid is used, lower results are obtained, *cf.* p. 253.

it is not evolved as hydrogen sulfide upon treatment with acid. This difficulty can usually be overcome by annealing the sample before analyzing it for sulfur.

The Bamber method is recommended in the United States for settling disputed analyses. The Bureau of Standards at Washington have had success with Method *d* although it is open to the theoretical objection that errors are involved, as already pointed out, in precipitating sulfuric acid in the presence of iron.

The first evolution method, Method *a*, gives excellent results but occasionally they are too low. It is slightly more reliable than the other evolution method because it provides for the oxidation of any gas containing sulfur.

The method based upon the removal of the ferric chloride by ether is probably as reliable as any method that has been proposed but is not used in busy laboratories on account of the time required for the analysis and on account of the unpleasantness and danger involved in constantly working with ether.

Accuracy of the Results.—Duplicate determinations should agree within 0.005 per cent. in the analysis of steels containing 0.2 to 0.4 per cent. sulfur and within 0.003 per cent. in the case of steels containing 0.015 per cent. sulfur or less.

2. DETERMINATION OF SULFUR IN INSOLUBLE MATERIALS

(Ferro-silicon, Ferro-chrome, Etc.)

The mixture of 1 part sodium carbonate and 2 parts magnesium oxide, known as *Eschka's mixture*, is suitable for determining a small sulfur content of an insoluble substance. The sample should be in the form of a fine powder and particular care should be taken to avoid contamination with sulfur in the atmosphere. The use of the gas flame, therefore, is prohibited. An alcohol burner may be used for the ignition but an electric furnace is even better. Ignite the insoluble material in a platinum dish with about 8 times as much Eschka's mixture until the oxidation of the sample is complete.

Transfer the ignited mass to a beaker and rinse the dish, using about 50 cc. of water. Add 15 cc. of saturated bromine water and boil 5 min. Allow the residue to settle, decant the solution

through a filter, boil a second and a third time with 30 cc. of water, and finally wash the residue with hot water until the filtrate shows no test for chloride. Add 3 cc. of hydrochloric acid (sp. gr. 1.1) and evaporate the solution to dryness to dehydrate silica. Take up the residue with 5 cc. of hydrochloric acid, dilute, filter and precipitate the sulfuric acid in the filtrate with a hot, dilute solution of barium chloride. Filter, ignite and weigh the precipitate of barium sulfate in the usual manner.

Test Analyses.—The sulfur was determined in a sample of ferro-silicon using a 2-g. sample and 15 g. of the Eschka mixture. Duplicate determinations agreed within 1 mg. of barium sulfate showing respectively 0.037 and 0.044 per cent. S.

CHAPTER VII

COPPER

Copper, to the extent of a few tenths of 1 per cent., is a common constituent of iron and steel. Often its presence is accidental but in some cases it is added intentionally for the purpose of preventing corrosion.

1. PRECIPITATION AS SULFIDE FROM ACID SOLUTION

Principle.—The solution containing ferrous chloride and cupric chloride in the presence of free hydrochloric acid is treated with hydrogen sulfide, which precipitates cupric sulfide. The precipitate is purified and the copper determined as oxide.

Procedure.—Dissolve 10 g. of the iron or steel in 100 cc. of hydrochloric acid (sp. gr. 1.12) in a beaker of about 500 cc. capacity. Heat on the water bath until all the metal is dissolved.

Instead of using a separate sample for this determination, the solution obtained in the determination of sulfur by the evolution method (p. 252) or the filtrate from the silicon determination may be taken.

When the metal is all dissolved, dilute the solution to about 200 cc.[1] and introduce hydrogen sulfide gas for half an hour. Then heat a short time on the water bath to expel most of the excess hydrogen sulfide and filter through a filter that runs rapidly. Wash the precipitate and filter with water containing hydrogen sulfide until all the hydrochloric acid has been removed, taking care during all the filtration and washing to keep liquid in the filter. This is important because copper sulfide oxidizes rapidly to copper sulfate on standing in the air and then washes through into the filtrate, causing a turbidity there. It is necessary to remove

[1] If the solution stands too long some of the iron is oxidized to the ferric condition which causes the precipitation of sulfur when hydrogen sulfide is introduced.

all the hydrochloric acid from the precipitate because otherwise some cupric chloride will be lost by volatilization during the next operation.

As soon as the washing is complete, transfer the precipitate to a large, unweighed porcelain crucible and smoke off the filter paper by means of a low flame, keeping the temperature as low as possible. Moisten the ash with concentrated nitric acid and heat again until the carbon is all consumed. To the residue, which now contains all the copper as black cupric oxide, add a few cc. of hydrochloric acid (sp. gr. 1.12) and heat until all the copper oxide is dissolved. Evaporate the solution to dryness, to render traces of silica insoluble, treat the residue with hydrochloric acid, dilute and filter into a small beaker of 100 to 150 cc. capacity. Wash the filter with water containing a little hydrochloric acid but avoid letting the filtrate exceed about 30 cc.

To precipitate the copper again, add 10 to 20 cc. of saturated hydrogen sulfide water and heat on the water bath with frequent stirring until the precipitate collects together and the supernatant liquid is clear. Filter through a small filter until all the hydrochloric acid is removed, using wash water containing hydrogen sulfide. Ignite the precipitate in a weighed porcelain crucible at a low temperature until all the carbon of the filter is consumed, cool in a desiccator and weigh as cupric oxide, CuO.

If care is not taken in igniting the copper sulfide precipitate, there is danger of mechanical loss.

The ignited and weighed cupric oxide should dissolve in hydrochloric acid without leaving a weighable residue; the addition of ammonia in excess should then give a clear, deep-blue solution.

In the analysis of cast iron containing considerable silicon and graphite, the silicon should be removed at the start by Method 1A, p. 169, and the copper precipitated as sulfide in the filtrate. The residue obtained after treatment of the silica with sulfuric and hydrofluoric acids should also be examined for copper.

Computation.—If p represents the weight of the copper oxide obtained from a sample of metal weighing s g. then

$$\text{per cent. Cu} = \frac{79.89 \times p}{s}$$

2. DETERMINATION AFTER REMOVAL OF IRON WITH ETHER

Principle.—By shaking with ether a hydrochloric acid solution containing considerable ferric chloride and a little cupric chloride, the greater part of the former salt dissolves in the ether while all of the latter salt remains in the aqueous layer.

Procedure.—Dissolve about 10 g. of the sample in dilute nitric acid (sp. gr. 1.2) and remove the silicon as described in Method 1B on p. 173. In the filtrate carry out the Rothe ether separation as described under Manganese, p. 185. The aqueous hydrochloric acid solution then contains only a little iron, but all of the copper manganese, nickel, chromium, etc. Evaporate the solution on the water bath to remove dissolved ether, take up the residue in a little hydrochloric acid, add water and filter the solution, if necessary, to remove traces of silica and titanium oxide. Precipitate the copper with hydrogen sulfide according to the procedure given in Method 1, cautiously ignite the precipitate in a porcelain crucible and weigh as cupric oxide, CuO.

3. REMOVAL OF THE IRON WITH SULFURIC ACID[1]

Principle.—In the potential series of the metals, iron has a greater and copper a smaller solution pressure than hydrogen. For this reason iron dissolves readily in dilute sulfuric acid while copper, in the absence of oxidizing agent, does not. To make sure that traces of copper are not dissolved, hydrogen sulfide water should be added to the solution before filtering.

Procedure.—Dissolve 10 g. of the sample in 75 cc. of dilute sulfuric acid, 10 per cent. by volume. Saturate the hot solution with hydrogen sulfide and filter. Wash the filter free from iron with very dilute sulfuric acid containing hydrogen sulfide. Incinerate the filter and its contents in a porcelain crucible, digest the ash with nitric acid and transfer the solution to a platinum crucible. Evaporate to dryness, heat the residue with sulfuric and hydrofluoric acids to remove silica, and finally expel the excess of acid. Digest the residue with a little sulfuric aid (1 vol. acid : 5 vols. water) and filter. If any residue remains, fuse it for a short time with a little potassium pyrosulfate $K_2S_2O_7$,[2] dissolve

[1] This method is recommended by the U. S. Bureau of Standards, Circular No. 14 (1913).

[2] Made by fusing $KHSO_4$ till all water is expelled.

the melt in water and add it to the solution previously obtained. The copper can then be determined as oxide, after previous precipitation as sulfide (*cf.* Method 1) or be deposited electrolytically (*cf.* Method 4).

4. ELECTROLYTIC DETERMINATION OF COPPER

Principle.—The first copper sulfide precipitate obtained in Method 1 or in Method 2, as well as the copper sulfate solution obtained in Method 3, may be used for the electrolytic determination of copper. The electrolytic deposition of copper can be accomplished successfully under quite varying conditions. For this reason the procedures described by different chemists often vary considerably. It is well to bear in mind, however, that too much acid prevents the deposition and too strong currents are likely to cause spongy deposits. In general, stronger currents can be employed with a gauze cathode than when a plate electrode is used.

Moreover, the more concentrated the solution and the larger the surface of cathode exposed, the stronger the current may be. Stirring, when accomplished by rotating one of the electrodes, by an electromagnetic effect in Frary's apparatus (p. 274), or in any other way, also shortens the time required for electrolysis by permitting the use of stronger currents.

Procedure.—In case the analysis is started as described in Method 1 or in Method 2, dissolve the ignited cupric oxide, obtained by igniting the sulfide precipitate, in a little nitric acid, add a few drops of sulfuric acid and evaporate until fumes of sulfuric anhydride are evolved. Cool, add enough water to dissolve all the copper sulfate and transfer the solution to a small beaker of not over 200 cc. capacity.

Dilute this solution, or that obtained in Method 3, to about 50 cc. and electrolyze with stationary electrodes and a current of about 0.2 ampere or, if a gauze cathode and stirring apparatus are available, a much stronger current may be employed and the analysis finished more quickly.

When all the copper is removed from the solution, which is usually the case at the end of 3 hr. with stationary electrodes, quickly detach the cathode and wash it immediately by

plunging it into water in a beaker. Rinse with alcohol, dry a short time at 100°, cool and weigh. Test the solution for copper by passing hydrogen sulfide into it. If any precipitate of copper sulfide is obtained, it may be filtered off, ignited in a porcelain crucible and weighed as cupric oxide, CuO, or the oxide may be dissolved in acid and the solution electrolyzed as before, using a clean electrode surface.

Accuracy of the Results.—With care, the copper content of a steel can be determined by any one of the above methods with an error of not more than 1 mg. in the final weight. Using a 10-g. sample this corresponds to an error of 0.01 per cent. If the quantity of copper in the steel is less than 0.2 per cent. duplicate determinations should agree within about 0.005 per cent.

5. THE RAPID DETERMINATION OF COPPER IN STEEL[1]

Principle.—This procedure is a modification of A. H. Low's method[2] for determining copper in ores. Copper is electronegative to aluminium in the potential series of metals and for this reason aluminium displaces copper when placed in the solution of a copper salt. Moreover, copper is lower than hydrogen in the series, so that hydrochloric and sulfuric acids do not dissolve copper in the absense of an oxidizing agent; if any copper dissolves the aluminium will precipitate it even in the presence of acid. The residual copper is dissolved by nitric acid, the solution is neutralized by ammonia, acidified with acetic acid and the cupric ions are changed to cuprous iodide by treatment with potassium iodide whereby an equivalent weight of iodine is set free:

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + 4KC_2H_3O_2 + I_2$$

The free iodine is titrated with standard sodium thiosulfate solution.

Solutions Required

1. *Standard Sodium Thiosulfate Solution.*—Dissolve 25 g. of pure, crystallized, sodium thiosulfate $Na_2S_2O_3.5H_2O$ in water and dilute the solution to 5 liters. The solution is approximately

[1] E. D. Koepping, J. Ind. Eng. Chem., **6**, 696 (1914).

[2] A. H. Low, "Technical Methods of Ore Analysis."

0.02 normal. Use water that has been recently boiled free from carbon dioxide and cooled. Standardize the solution against 10 cc. of tenth-normal potassium permanganate solution (p. 206), against about 0.1 g. of pure iodine (p. 287), or against metallic copper.

To standardize against pure metallic copper, dissolve about 0.1 g. of pure copper,[1] in a 200 cc. Erlenmeyer flask with 5 cc. of a mixture of equal parts nitric acid (sp. gr. 1.42) and water. Dilute the solution to 25 cc. and boil a few minutes to remove oxides of nitrogen. To remove the last traces of nitrous acid, add 5 cc. of bromine water and boil until the excess bromine is expelled. Cool somewhat and add strong ammonia until a slight excess is present. Boil off the excess ammonia and add 7 cc. of strong acetic acid, which dissolves any copper oxide that may have been deposited by boiling the blue ammoniacal copper solution. Cool to room temperature, add 2 g. of pure potassium iodide, and titrate with sodium thiosulfate until nearly colorless. Then add 2 cc. of starch solution (0.5 g. of soluble starch dissolved in 25 cc. of boiling water; the starch solution should cool before using it) and finish the titration.

In making the titration for the first time, it should be borne in mind that cuprous iodide is not white.

The reactions that take place during the standardization may be expressed as follows:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$NO + O = NO_2$$
$$2NO_2 + H_2O = HNO_2 + HNO_3$$
$$HNO_2 + Br_2 + H_2O = HNO_3 + 2HBr$$
$$Cu^{++} + 6NH_3 = Cu(NH_3)_6^{++}$$
$$Cu(NH_3)_6^{++} + 6H^+ = Cu^{++} + 6NH_4^+$$
$$Cu^{++} + 2I^- = CuI + I$$
$$2S_2O_3^- + I_2 = S_4O_6^- + 2I^-$$

Procedure.—Weigh from 3 to 10 g. of the metal, according to the probable copper content, into a small beaker and dissolve in 35 cc. of 6-normal hydrochloric acid (sp. gr. 1.12) or sulfuric acid

[1] This will require about 80 cc. of the dilute sodium thiosulfate solution.

(sp. gr. 1.18). Dilute the solution with 35 cc. of water and introduce a strip of aluminium foil, bent so that it will not lie flat on the bottom of the beaker, and boil the solution for 20 min.

Remove the beaker from the hot plate and wash down the cover glass and sides of the beaker with hot water. Filter through a 11 cm. filter and wash the residue promptly with hot water. Puncture the filter, and rinse the precipitated copper into a 30 cc. Erlenmeyer flask. Cover the aluminium, in the original beaker in which the copper was deposited, with a mixture of 3 cc. concentrated nitric acid (sp. gr. 1.42) and 7 cc. of water and pour the acid through the pierced filter. Finally wash the aluminium and the filter with hot water. Boil the copper nitrate solution a few minutes to remove nitrous fumes, cool somewhat, and then add 7 cc. of strong ammonia (sp. gr. 0.90). Boil until the deep blue solution becomes pale blue and the ammonia odor is faint. Add 10 cc. of 80 per cent. acetic acid and boil 1 min. more. Allow the solution to cool and when at the room temperature, or colder, add 3 gr. of potassium iodide and at once titrate the liberated iodine with the sodium thiosulfate solution.

Computation.—If in the standardization of the solution, n_1 cc. of thiosulfate were required for e_1 g. of copper, then

$$1 \text{ cc. } Na_2S_2O_3 = \frac{e_1}{n_1} = T \text{ g. copper}$$

If the solution was standardized against 10 cc. of a-normal permanganate, and n_2 cc. of thiosulfate were required; then

$$1 \text{ cc. } Na_2S_2O_3 = \frac{10a \times 0.06357}{n_2} = T \text{ g. copper}$$

If standardized against pure iodine, and e_3 g. of iodine required n_3 cc. of solution,

$$1 \text{ cc. } Na_2S_2O_3 = \frac{e_3}{n_3} \cdot \frac{0.06357}{0.1269} = T \text{ g. copper}$$

If n cc. of thiosulfate solution were required in the analysis of s g. of steel, then

$$\text{per cent. Cu} = \frac{100n.T}{s}$$

CHAPTER VIII

NICKEL

Nickel, in traces at least, is a very common constituent of iron and steel. It is rarely present much in excess of 0.1 per cent. except when it is intentionally added in special steels.

Three methods for the determination of this element will be described, the dimethylglyoxime method, the electrolytic method, and the volumetric method. Of these methods only the first mentioned is uninfluenced by the presence of cobalt which almost invariably accompanies nickel. Usually the cobalt content is in the neighborhood of 1 per cent. of the nickel content; the results obtained by the last two methods should be correspondingly higher.

1. DETERMINATION OF NICKEL BY THE DIMETHYLGLYOXIME METHOD

Principle.—From a nearly neutral solution, it is possible to precipitate nickel quantitatively by the addition of dimethylglyoxime[1] in alcoholic solution. The method was first used by Tschugaeff[2] for the qualitative detection of traces of nickel and was perfected by Brunck for quantitative work.[3] Dimethylglyoxime, also called *diacetyldioxime*, has the following constitutional formula:

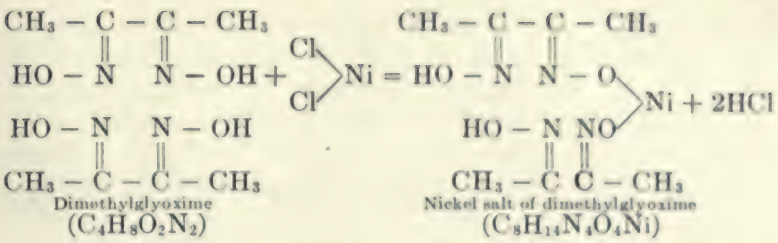
$$\begin{array}{ccccc} CH_3 & - & C & - & C & - & CH_3 \\ & & \| & & \| & & \\ HO & - & N & & N & - & OH \end{array}$$

which corresponds to the empirical formula ($C_4H_8O_2N_2$). One atom of nickel replaces 2 atoms of hydrogen in 2 molecules of dimethylglyoxime; the reaction may be written:

[1] This substance was expensive until a demand arose for it as reagent. In 1908 the price was reduced to about 30 cents a gram but in 1911 it cost only about 4 cents a gram.

[2] Ber., **38,** 2520 (1905).

[3] Z. angew. chem., **20,** 1844 (1907).



The precipitation may be accomplished in the presence of other metals, such as copper, cobalt, chromium, iron, manganese, tungsten and vanadium, provided a sufficient quantity of tartaric acid is present to prevent any precipitation of these elements by means of ammonia. The reagent is not very soluble in water and for this reason care must be taken not to use too large an excess, or the results will be too high.

Requisite Solutions. *Dimethylglyoxime Solution.*—Dissolve 10 g. of dimethylglyoxime in 1 liter of 98 per cent. alcohol and filter if necessary. Ten cubic centimeters of this solution will precipitate approximately 0.025 g. of nickel.

Tartaric Acid Solution.—Dissolve 500 g. of tartaric acid in 1 liter of water and filter if necessary; 14 cc. of this solution require about 17 cc. of ammonia (sp. gr. 0.96), for neutralization.

Procedure.—Take 1 g. of a nickel steel containing 3 to 5 per cent. nickel or 2 g. if the steel contains little nickel.[1] Dissolve the sample, in a porcelain casserole, in nitric acid (sp. gr. 1.2) and while the sample is dissolving and the evolution of gases is likely to result in mechanical losses, keep the casserole covered with a watch-glass. Evaporate the solution to dryness, ignite the residue carefully until the nitrates are decomposed and then treat it with 20 cc. of concentrated hydrochloric acid (sp. gr. 1.2) heating until all the ferric oxide is dissolved. Evaporate the solution once more to dryness, take up in a little hydrochloric acid, dilute and filter off the silica,[2] receiving the filtrate in a 300 cc. beaker.

To the filtrate add 14 cc. of the tartaric acid solution for each g. of iron present and dilute ammonia until the solution is slightly

[1] *cf.* p. 273. Note 2.

[2] If the silica is not removed, it may contaminate the nickel precipitate, especially with steels high in silicon.

ammoniacal. Often a yellow precipitate of basic ferric tartrate is obtained when the solution is neutral but this precipitate will dissolve upon the addition of a little more ammonia. When distinctly ammoniacal there should be no precipitate in the brown solution. If a precipitate is present it indicates too little tartaric acid. Make the solution barely acid with hydrochloric acid, heat it nearly to boiling and add 20 cc. of the alcoholic solution of dimethylglyoxime, and then ammonia until, after stirring and blowing away the vapors, a faint odor of ammonia can be detected above the solution. Any nickel present will be precipitated in the form of fine red needles.[1] After allowing the solution to stand a little while, add 10 cc. more of the dimethylglyoxime solution to see if any further precipitation takes place. If this is the case, it may be necessary to add still more of the reagent.

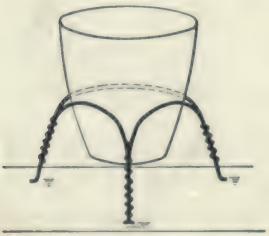


FIG. 128.

Allow the solution to stand in a warm place for 1 hr. and then allow to cool for about half an hour.

Meanwhile prepare a Munroe or Gooch crucible (p. 193), place it in a platinum or nichrome triangle (Fig. 128), heat it at 120° for 1 hr., cool in a desiccator and weigh. Filter the solution through this weighed crucible, using gentle suction. Take care to keep liquid in the crucible and not let the crystals get packed too closely on the asbestos felt, as this interferes with the filtration. Use as gentle suction as will permit rapid filtration. Wash the precipitate with hot water till free from iron (8 to 12 times) and then allow it to drain. Place the crucible in a platinum or nichrome triangle, such as is shown in Fig. 128, and heat in a hot closet at 120° for at least half an hour. Cool in a desiccator and weigh. Heat again in the hot closet to see if the weight is constant.

To clean the crucible, pick out the greater part of the precipitate without interfering with the asbestos felt, wash with hot dilute hydrochloric acid, then with water and dry at 120°, after which the crucible is ready for use again.

[1] If precipitation takes place in the cold, the precipitate is of a slightly different character and filters less readily.

Computation.—If p g. of nickel precipitate were obtained in the analysis of s g. of steel then

$$\text{per cent. Ni} = \frac{20.32\ p}{s}$$

NOTES.—1. It is not advisable to attempt to work with too large a nickel precipitate. The weight of sample should be regulated so that the quantity of nickel to be precipitated shall not exceed 0.05 to 0.08 g. Instead of weighing out a very small sample when the alloy is rich in nickel, it is usually better, for the sake of getting a good average sample, to dissolve 2 or 3 g. of the original material and then take an aliquot part for the final precipitation.

Thus, with a steel containing 25 per cent. of nickel, weigh out 3 g. of the material, dilute the solution to 500 cc. in a calibrated flask, thoroughly mix by pouring back and forth several times into a dry beaker, and then take 50 cc. (= 0.3 g. of the sample) for the precipitation with dimethylglyoxime.

2. If the nickel content is less than 0.1 per cent., it is not advisable to attempt to carry out the precipitation of the nickel in the presence of all the iron. In such cases, carry out the Rothe ether separation, as described on p. 185 for the separation of iron from manganese, and then proceed as described above using only 5 cc. of the tartaric acid solution. Or, in case it is desired to determine other elements in the hydrochloric acid solution, the nickel may be precipitated by hydrogen sulfide in acetic acid solution, the precipitate dissolved in a little aqua regia, the free chlorine boiled off, the solution diluted, and the nickel then precipitated with dimethylglyoxime and a slight excess of ammonia.

3. In the analysis of nickel-plated iron and steel, it is often desired to know the depth of the nickel coating. In such cases, dissolve the nickel coating from one or several pieces, the surface area of which has been accurately measured, in cold nitric acid (sp. gr. 1.42), pour off the nickel solution into a second beaker, wash the metal several times with strong nitric acid, evaporate off the excess of acid, add tartaric acid solution and proceed in the usual way to determine the nickel.

Assuming the specific gravity of nickel to be 8.9, the surface of the samples examined to be s sq. mm., and the weight of the nickel precipitate p g., then d, the thickness of the nickel coating, is given by the equation:

$$d = \frac{0.2032\ p}{8.9s}$$

4. *Recovery of Dimethylglyoxime from Nickel Precipitates.*—Triturate the precipitates with a little water in a mortar, rinse the paste into a porcelain evaporating dish and heat, with the addition of a little potassium cyanide, until the nickel salt dissolves forming a reddish-yellow solution. Filter the solution, before letting it stand very long, through a plaited filter to remove asbestos fibers and other insoluble material. Allow the solution to cool and saturate it with pure carbon dioxide gas. At the end of an hour all the dimethylglyoxime will be precipitated. Filter it off on a Büchner suction funnel, wash with cold water, dry and weigh. Dissolve the dry powder in alcohol, using 100 cc. for each gram of the powder, add a little bone black, heat and filter. The clear solution is now ready for use as reagent.

2. DETERMINATION OF NICKEL BY ELECTROLYTIC DEPOSITION

Principle.—After the removal of the greater part of the iron, preferably by the Rothe ether separation, and the precipitation of the copper as sulfide from acid solution, the nickel may be deposited electrolytically from an ammoniacal solution containing ammonium sulfate.

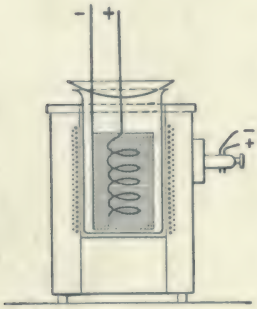


FIG. 129.

Apparatus.—The analysis may be carried out with a platinum spiral as anode and a platinum plate electrode as cathode, but the time required may be shortened by using a cylinder of platinum gauze as cathode, which permits the use of a stronger current. Stirring the electrolyte is also helpful and this can be accomplished very satisfactorily in the Frary apparatus,[1] Fig. 129, which is based upon the principle of the solenoid and causes, by the magnetic influence of the current in the coil of wire in the apparatus, the rotation of the electrolyte while the current is being passed through it. The platinum gauze electrode is required in this apparatus, as it allows the electrolyte to stream through it. The movement of the electrolyte is not satisfactory when a solid electrode is used. In all cases, there is less danger of obtaining spongy deposits with gauze electrodes.

Procedure.—Dissolve 3 to 5 g. of an ordinary nickel steel,

[1] Z. Elektrochemie, **13**, 308 (1907); J. Am. Chem. Soc., **29**, 1592 (1907).

or 5 to 10 g. of a steel with low nickel content, in nitric acid, and prepare the solution for the ether separation exactly as described under Manganese, p. 185.[1]

After the removal of the iron by the ether, evaporate the solution to expel the dissolved ether and precipitate the copper as sulfide according to p. 263. Boil the filtrate to expel hydrogen sulfide, add a little sulfuric acid and evaporate until the excess of sulfuric acid is expelled. Treat the residue with sodium hydroxide and sodium peroxide to remove chromium as described under Manganese, p. 189.[2]

After washing out the sodium chromate and other sodium compounds, dissolve the oxides (chiefly of nickel, cobalt, manganese and residual iron) by heating with hydrochloric acid (sp. gr. 1.12). Dissolve any residue in the platinum dish with a crystal of oxalic acid and a little sulfuric acid, and add the solution to that already obtained. If considerable manganese is present, it is best to neutralize the solution with ammonia, acidify it slightly with acetic acid and precipitate the nickel and cobalt with hydrogen sulfide. Filter off the sulfide precipitate and ignite it in a porcelain crucible. Dissolve it in a little aqua regia and prepare the solution for electrolysis as described below. Small quantities of manganese do no harm and in such cases it is unnecessary to precipitate the nickel and cobalt as sulfides. Add a slight excess of sulfuric acid to the hydrochloric acid solution and evaporate until fumes of sulfuric anhydride are evolved. Add a little water and transfer the solution to a beaker of about 150 cc. capacity which fits in the Frary apparatus. Add 5 g. of solid ammonium sulfate and 20 to 30 cc. of strong ammonia in excess of the quantity required to neutralize the solution. Dilute to about 100 cc., place the beaker in the Frary apparatus and connect the electrodes, as well as the Frary apparatus itself, with the source of electricity. With a current of 5 amperes passing through the solution and a current of about the same strength through the coil, the nickel

[1] The rapid method described on p. 200 may be used for the removal of the silica.

[2] If chromic salts are present during the electrolysis, they are oxidized to chromate and interfere somewhat with the deposition of nickel. The addition of sodium hypophosphite to the bath before electrolysis is recommended when a little chromium is present.

and cobalt should all be deposited in less than half an hour. In case the gauze electrode is used with a stationary electrolyte, a current of 0.7 to 1.0 ampere should cause complete deposition in 1 hr. To make sure that the electrolysis is complete, add a little water and note whether any deposition of metal takes place on the freshly exposed electrode surface. If this is not the case, withdraw a few drops of the solution by means of a pipette and add it to a drop of ammonium sulfide on a porcelain spot plate. If no brown precipitate is obtained, the deposition is complete. Disconnect the cathode, quickly withdraw it from the solution and at once transfer it to a beaker containing hot water to free it from adhering ammonium salt. Rinse off the water with alcohol, dry the electrode a short time at 110°, cool and weigh.

The deposited nickel contains any cobalt that may have been present in the sample.

Test Analyses

(*a*) *Pure Nickel Solution.*—Duplicate electrolytic determinations with 50-cc. portions gave the values 0.1504 g. and 0.1501 g. Ni. Three portions of the same solution were analyzed by the dimethylglyoxime method and the values 0.1502, 0.1505, and 0.1503 g. Ni were obtained.

Two 10-cc. portions of the same nickel solution (0.0301 g. Ni) were each mixed with 50 cc. of pure ferric chloride solution (4.8 g. Fe) and to one portion 25 cc. of manganous chloride solution (0.6 g. Mn) was also added. The nickel was then determined in each solution by adding tartaric acid and dimethylglyoxime with the usual precautions. The values 0.0305 g. and 0.0303 g. Ni were obtained.

(*b*) *Experiments with Nickel Steel.*—Using a sample weighing 0.5 g., the dimethylglyoxime method gave 22.88 per cent. Ni, and with 0.2088 g. of the steel the value 23.00 per cent. Ni.

Using the electrolytic method and samples weighing respectively 1.000, 3.611, and 3.861 g., the values 23.40, 23.50, and 23.46 per cent. Ni were obtained.

The difference between the values obtained by the two methods was due to the fact that the steel contained about 0.51 per cent. of cobalt.

(*c*) *Determination of Nickel by the Dimethylglyoxime Method in Various Samples of Commercial Steel.*—Five samples of steel and cast iron with nickel content ranging from 0.01 to 5.05 per cent. were analyzed and in all cases duplicates agreed within 0.01 per cent.

Accuracy of the Values and Permissible Deviations

Owing to the fact that the cobalt content of different steels varies considerably, it often happens that the results obtained by the dimethylglyoxime method are considerably lower than those obtained by electrolysis.

If it is desired to know the content of pure nickel, the dimethylglyoxime method is the better method; the electrolytic deposition of the two metals followed by the determination of the cobalt is a much more tedious operation.

The variations in the weights of precipitate in duplicate determinations with dimethylglyoxime should rarely vary more than 1 or 2 mg. When less than 5 per cent. of nickel is present, the determinations should agree within 0.02 per cent. and within 0.005 per cent. if less than 1 per cent. of nickel is present.

3. VOLUMETRIC DETERMINATION OF NICKEL BY POTASSIUM CYANIDE[1]

Principle.—When an excess of ammonia is added to a solution containing nickel ions, a pale blue nickel-ammonia complex cation is formed. Thus with nickel chloride the reaction may be written:

$$NiCl_2 + 6NH_3 = [Ni(NH_3)_6]Cl_2$$

This complex nickel-ammonia ion, $Ni(NH_3)_6^{++}$, is fairly stable in solutions containing ammonia, but on adding potassium cyanide a much more stable anion, $Ni(CN)_4^{=}$, is formed

$$[Ni(NH_3)_6]Cl_2 + 4KCN = K_2[Ni(CN)_4] + 6NH_3 + 2KCl$$

[1] *cf.* Campbell and Andrews, J. Am. Chem. Soc., **17,** 126 (1895); Moore, Chem. News, **72,** 92 (1895); Goutal, Z. angew. Chem., **1898,** 177; Brearley and Jarvis, Chem. News, **78,** 177 and 190; Johnson, J. Am. Chem. Soc., **29,** 1201 (1907); Campbell and Arthur, *ibid.*, **30,** 1116 (1908); Grossmann, Chem.-Ztg., **32,** 1223 (1908).

The stability of this nickelo-cyanide ion is so great, and its tendency to dissociate into simple nickelous cations and cyanide anions is so slight, that potassium cyanide will not react with insoluble silver iodide until all of the nickel-ammonia ions have disappeared. If, then, the solution originally contained some suspended silver iodide, this insoluble compound will react with potassium cyanide, after all the nickel-ammonia ions have disappeared, in accordance with the equation:

$$AgI + 2KCN = K[Ag(CN)_2] + KI$$

The stability of this argenticyanide is also very great. The reason why the potassium cyanide reacts with the nickel-ammonia cations rather than with silver can be traced to the fact that more free nickel ions are present in a slightly ammoniacal solution than there are dissolved silver ions in the liquid which is in contact with precipitated silver iodide.

If, after all the nickel and silver have reacted with the potassium cyanide to form complex anions, a little silver nitrate is added, it reacts with the potassium iodide to form a precipitate of silver iodide.

$$KI + AgNO_3 = AgI + KNO_3$$

The volumetric determination of nickel by means of potassium cyanide consists in adding potassium cyanide to a nickel-ammonia solution containing a known quantity of silver iodide until the precipitate dissolves, and then adding just enough more silver to produce a turbidity again. By deducting the volume of potassium cyanide required to react with the silver from the total volume used, the volume of potassium cyanide required to react with the nickel is known.

The method can be carried out in the presence of most of the other elements of the ammonium sulfide group. If copper is present in quantities not exceeding 0.4 per cent., the copper will replace almost exactly three-quarters of its weight of nickel.

When cobalt is present, the solution assumes a dark color upon the addition of potassium cyanide, but if not more than one-tenth of 1 per cent. of this element is present in the

original sample, the titration can be carried out successfully and the results represent the amount of nickel and cobalt present.

The determination may take place even in the presence of iron if a considerable quantity of citric acid or tartaric acid is first added to the solution. The citric or tartaric acid prevents the precipitation of the iron by ammonia. A dark-colored solution results and the end point cannot be distinguished readily unless a large excess of the organic acid is added. This will also prevent interference by chromium present as chromic salt.

Necessary Solutions. *Potassium Cyanide Solution.*—A convenient strength is to make it approximately equivalent to tenth-normal silver nitrate. Since 1 atom of silver reacts with 2 molecules of potassium cyanide, it follows that a tenth-normal solution of potassium cyanide for this analysis should contain one-fifth of a mole dissolved in a liter. To prepare the solution, therefore, dissolve 13.5 g. of pure potassium cyanide in water, add 5 g. of potassium hydroxide dissolved in water, and dilute the solution to 1 liter. Potassium cyanide containing sulfide cannot be used; it forms a precipitate of silver sulfide with the silver added and silver sulfide is not dissolved by potassium cyanide.

Tenth-normal Silver Nitrate Solution.—Dissolve exactly 8.495 g. of pure silver-nitrate crystals, that have been powdered and dried half an hour at 105°, and dilute the solution to exactly 1 liter in a calibrated flask.

Potassium Iodide Solution.—Dissolve 2 g. of potassium iodide in 100 cc. of water.

To standardize the potassium cyanide solution, measure out about 30 cc. of it from a burette, dilute to about 100 cc., add 5 cc. of potassium iodide solution, and titrate with silver nitrate until a faint permanent opalescence is obtained. The opalescence should be so slight that it can be cleared up by a small drop of potassium cyanide solution. The reactions that take place are as follows:

$$2KCN + AgNO_3 = KAg(CN)_2 + KNO_3$$
$$KI + AgNO_3, = AgI + KNO_3$$

If any AgI is formed before the first reaction is finished it dissolves,

$$AgI + 2KCN = KAg(CN)_2 + KI$$

The end-point is sharper when potassium iodide is present. Without it, a slight excess of $AgNO_3$ would react with the complex cyanide as follows:

$$KAg(CN)_2 + AgNO_3 = KNO_3 + 2AgCN$$

Procedure.—Dissolve 1 g. of steel in a casserole with 10 to 50 cc. of nitric acid (sp. gr. 1.2), adding a little hydrochloric acid if necessary. After the steel has dissolved, add 6 or 8 cc. of sulfuric acid, diluted with an equal volume of water, and evaporate until fumes of sulfuric acid are evolved. Cool, add 30 to 40 cc. of water and boil the contents of the casserole until all the ferric sulfate has dissolved. Transfer the solution to a 400-cc. beaker, dilute to about 300 cc. and add 12 g. of powdered citric acid, or, if chromium is present, add twice as much citric acid. When the citric acid has all dissolved make the solution faintly but distinctly alkaline with ammonia.

As the ammonia is added the color of the solution changes. The solution turns green, then yellow, and finally assumes a brownish shade when the ammonia is present in excess. With the large amount of citric acid used, the color is not such a deep red as when only a little is present.

To the cold solution, which is alkaline to litmus but does not contain a large excess of ammonia, add about 2 cc. of the potassium iodide solution and enough of the tenth-normal silver nitrate from a burette to produce a distinct turbidity. About 0.5 cc. of silver nitrate is sufficient. The solution is now ready for titration with potassium cyanide.

Add the potassium cyanide solution, while stirring constantly, until the precipitate of silver iodide disappears. Then finish the titration by adding just enough silver nitrate to cause the formation of a very slight turbidity.

Computation.—If 1 cc. of potassium cyanide solution is equivalent to t cc. of tenth-normal silver nitrate solution, and n_1 cc. of silver nitrate together with n_2 cc. of potassium cyanide are used in the analysis of a sample of steel weighing s g., then

$$\text{per cent. Ni} = \frac{(n_2 t - n_1)\, 0.2934}{s}$$

NOTE.—The temperature of the solution should not be much above 20° during the titration. Too large an excess of ammonia should not be present as it tends to impede the course of the reaction by making the nickel-ammonia complex more stable so that it is not decomposed readily by the potassium cyanide.

The method is often used after the removal of the iron by the ether method. It is then easier to carry out the titration. The results are accurate.

CHAPTER IX

COBALT

Cobalt is usually present to some extent in all samples of iron and steel that contain nickel. In some special cases this element is an intentional constituent.

DETERMINATION OF COBALT AS SULFATE

Principle.—The complex thiocyanates of nickel and cobalt may be separated from one another by treatment with a mixture of amyl alcohol and ether.[1]

Apparatus and Solutions Required

1. *Rothe shaking funnel* (Fig. 120, p. 184).

2. *Amyl alcohol-ether* mixture. Mix 25 parts by volume of ether with 1 part of amyl alcohol.

Procedure.—If the nickel content is fairly high, weigh out about 5 g. of the original metal, or 10 g. if the nickel content is low. Deposit the nickel and cobalt electrolytically, as described on p. 274, and weigh the deposit.

Dissolve the deposited nickel and cobalt in a little concentrated nitric acid (sp. gr. 1.42) and carefully rinse off the electrode. To remove the excess of acid, evaporate the solution of nickel and cobalt nitrates just to dryness in a porcelain dish and dissolve the residue in a little water. For each 0.1 g. of metal present, add 4 g. of pure ammonium thiocyanate, NH_4CNS[2], to the concentrated solution of cobalt and nickel nitrates. Dissolve the salt by means of a little water. It is essential to have a

[1] Rosenhain and Huldschinsky (Ber., **34**, 2050 (1901)) first proposed the quantitative application of Vogel's sensitive test for cobalt in the presence of nickel (Ber., **12**, 2314 (1879)).

[2] Commercial ammonium thiocyanate is often impure. It is absolutely necessary that no weighable residue should be obtained on heating the salt.

saturated solution at this point; if necessary, concentrate it by evaporation on the water bath. Transfer the concentrated solution to the upper bulb of the Rothe shaking funnel and rinse out the evaporating dish with a little saturated ammonium thiocyanate solution. Then add 60 to 80 cc. of the amyl alcohol-ether mixture and shake vigorously. After the mixture has become perfectly quiet, the upper layer in the funnel is a beautiful blue even when only a little cobalt is present.[1] The cobalt is present in the ether layer as complex ammonium cobalto-thiocyanate and the nickel remains in the aqueous solution as simple thiocyanate. Allow the lower layer in the upper bulb of the funnel to run into the lower bulb and rinse the former with a little saturated ammonium thiocyanate solution. Add 10 cc. more of saturated ammonium thiocyanate solution to the contents of the upper bulb and 40 cc. of the ether mixture to the lower bulb and again shake vigorously. In this way the remainder of the nickel in the upper bulb is washed away from the ether and a little cobalt in the lower bulb is dissolved by the ether. Allow the liquids to stand until two layers are well separated in each bulb, and then transfer the green nickel solution in the lower bulb to a beaker and wash out the stopcock boring, etc., with a little ammonium thiocyanate solution. Then transfer the aqueous layer in the upper bulb to the lower bulb, and rinse the upper bulb with a little ammonium thiocyanate solution. Add 5 or 10 cc. of dilute sulfuric acid (1:10) to the upper bulb, close the stopcock and shake well. The blue color of the amyl alcohol-ether mixture will now disappear and the cobalt will pass into the dilute sulfuric acid solution, imparting a pink color to it. The aqueous thiocyanate solution in the lower bulb contains traces of nickel. Allow it to flow into the beaker and rinse the bulb in the usual manner. Then transfer the cobalt sulfate solution in the upper bulb into the lower bulb and rinse the ether-alcohol remaining in the upper bulb with a few drops of dilute sulfuric acid. By shaking, the blue ether solution in the lower bulb is now decolorized.[2] Transfer the sulfuric acid solution of cobalt sulfate to a weighed

[1] If a little iron is present the red color of ferric thiocyanate causes a composite colored layer and the iron contaminates the final cobalt sulfate.

[2] Usually the ether is colored reddish-brown by a little ferric thiocyanate.

porcelain crucible, rinse the ether-alcohol mixture in each bulb with small portions of dilute sulfuric acid and add the washings to the contents of the crucible. Evaporate to dryness and heat to destroy organic matter and finally to remove the excess of sulfuric acid, as described under Manganese, p. 188. Weigh the pink cobalt sulfate and then test it for impurities. Dissolve it in a little water and add ammonia until the solution is weakly ammoniacal. If a precipitate of ferric hydroxide is formed, filter it off and weigh it. Add dimethylglyoxime solution, drop by drop, as long as any precipitate continues to form. Allow the solution to stand half an hour in a warm place and then filter off the precipitate of nickel salt upon a small filter. Wash it thoroughly with hot water, ignite it and weigh as nickelous oxide, NiO.

The quantity of cobalt present is computed by deducting from the original weight of cobalt sulfate, the weight of ferric oxide[1] obtained, and of nickel sulfate corresponding to the weight of oxide obtained after igniting the glyoxime precipitate.

To weigh the cobalt itself after purification, evaporate the filtrate from the nickel precipitate in a weighed porcelain crucible, ignite the residue after moistening it with a little nitric acid and a drop of sulfuric acid, and heat to constant weight as described under Manganese, p. 195. Or, the cobalt sulfate solution may be dissolved in water and the ammoniacal solution electrolyzed as described under Nickel, p. 274.

Computation.—If p represents the weight of pure cobalt sulfate obtained in the analysis of s g. of metal, then

$$\text{per cent. Co} = \frac{38.03\ p}{s}$$

Test Analyses. 1. *Separation of Nickel and Cobalt in Solutions of Pure Salts.*—Twenty-five-cubic-centimeter portions of a nickel chloride solution containing 0.0245 g. nickel were mixed with 25-cc. portions of cobalt chloride solution containing 0.0110 g. cobalt. The cobalt was determined as sulfate according to the above directions and in three experiments the results obtained were 0.0115 and 0.0114 and 0.0122 g. cobalt. The cobalt sulfate

[1] Ferric sulfate changes to ferric oxide and sulfuric anhydride at temperatures at which nickel, cobalt and manganese sulfates are more stable.

obtained in the third experiment was impure. It was dissolved and the ammoniacal solution electrolyzed; 0.0114 g. cobalt was then obtained.

2. *Analysis of Nickel Steel.*—The nickel and cobalt were determined together by the electrolytic method described on p. 274. The results of two experiments gave the values 23.50 and 23.46 per cent. Ni + Co. From the electrolytic deposit, the impure cobalt sulfate obtained by the above method indicated 0.66 and 0.67 per cent. Co but after dissolving the sulfate and determining the cobalt electrolytically the results were 0.38 and 0.39 per cent. Co. The values obtained by deducting the weight of the nickel as determined by precipitation with dimethylglyoxime from the weight of the cobalt and nickel deposit, averaged 0.51 per cent.

3. *Cobalt Content of Commercial Nickel*.—Duplicate determinations of the cobalt content of a sample of commercial nickel gave the values 0.88 and 0.89 per cent. cobalt.[1]

[1] Commercial nickel sometimes contains a little zinc. This will come down with the cobalt in the electrolytic determination and will also follow the cobalt in the potassium thiocyanate separation.

CHAPTER X

CHROMIUM

Chromium to some extent, though not usually more than 0.1 per cent., is present in nearly all samples of iron and steel. Special steels are prepared by the addition of chromium, or chromium alloy, to steel; in this way chrome, chrome-nickel, silicon-chrome, chrome-tungsten and chrome-vanadium steels are prepared. In the preparation of these steels, ferrochrome and chrome-manganese are used chiefly. The chromium content of these two alloys varies considerably.

1. DETERMINATION OF CHROMIUM IN MATERIALS SOLUBLE IN ACID

(a) Ether Method

Principle.—In the trivalent condition, chromium, like manganese, nickel, cobalt and aluminium, may be separated from ferric iron by shaking the hydrochloric acid solution, of suitable concentration, with ether. In the solution which has been freed from the greater part of the iron, the trivalent chromic ions may be oxidized to hexavalent chromic acid ions and the chromium can then be determined either gravimetrically or volumetrically.

Necessary Apparatus and Solutions.—The necessary apparatus and solutions including the Rothe shaking funnel, ether-hydrochloric acid solutions, and platinum dish, have already been described under Manganese, p. 185.

According to the method chosen for the final determination of the chromium, various other solutions are necessary. If the chromium is to be determined iodometrically, a standardized tenth-normal solution of sodium thiosulfate is needed; if it is to be determined by the permanganate method, standardized solutions of potassium permanganate and ferrous sulfate are necessary. To determine the chromium gravimetrically, the method to be described requires a solution of mercurous nitrate.

Preparation and Standardization of Tenth-normal Sodium Thiosulfate Solution

Dissolve 124.5 to 125 g. of pure sodium thiosulfate crystals, $Na_2S_2O_3.5H_2O$, in water that has been boiled to expel carbonic acid and then cooled. The solution may be standardized against potassium permanganate solution which has been titrated against pure sodium oxalate. The procedure is the same as was described under Manganese, p. 206, for the standardization of permanganate against iodine solution. Another excellent method of standardizing the thiosulfate solution is to titrate it against pure iodine.

To prepare the pure iodine, mix 5 to 6 g. of pure, commercial iodine crystals with 2 g. of potassium iodide,[1] place the mixture in a dry beaker of 150–300 cc. capacity and cover the beaker with a 300 cc. round-bottomed flask, filled with water at the room temperature. Heat the bottom of the beaker over wire gauze by means of a small gas flame. In a short time the greater part of the iodine will have sublimed from the bottom of the beaker and will have condensed upon the colder bottom of the round-bottomed flask. Scrape the iodine crystals into a fresh beaker and repeat the sublimation without the use of potassium iodide, in order to get a perfectly pure product. Break up the crystals obtained by the second sublimation by pressing them with a pestle in an agate mortar, place them on a watch-glass and dry in a desiccator over calcium chloride for 24 hr; the top of the desiccator should not be greased.[2]

Place 2 g. of pure potassium iodide and not over 0.5 cc. of water in a small glass-stoppered weighing tube and weigh carefully to 0.1 mg. Open the stopper and introduce about 0.5 g. of the purified and dried iodine, which dissolves quickly in the concentrated potassium iodide solution, insert the stopper and weigh again.

Hold the weighing tube over a 500 cc. Erlenmeyer flask containing about 1 g. of pure potassium iodide dissolved in 200 cc.

[1] The iodide should be free from iodate, as shown by dissolving a little of it and adding a little pure hydrochloric acid; no iodine should be set free to color starch solution.

[2] Grease is likely to be attacked by the iodine vapor forming hydriodic acid which may contaminate the iodine crystals.

of water. Open the stopper of the weighing tube and at once drop the tube and its contents into the dilute potassium iodide solution. In this way there is no chance of losing an appreciable quantity of iodine by vaporization. Titrate the iodine with tenth-normal sodium thiosulfate until the iodine color fades to a pale yellow, then add 2 cc. of freshly prepared starch solution[1] and continue adding the sodium thiosulfate solution, drop by drop, till the blue color just disappears.

During the titration, the following reaction takes place:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

If the sodium thiosulfate solution is exactly tenth-normal, 1 liter of it will react with exactly one-tenth the atomic weight of iodine, or 1 cc. is equivalent to 0.01269 g. iodine. It is usually not worth while to make the solution exactly tenth-normal. By dividing the weight of iodine neutralized by 1 cc. by 0.1269, the relation of the solution to the normal solution can be obtained and this value may be called the *normality* of the solution. The inconvenience resulting from the use of such a fraction is very slight.

The reaction between the chromate and iodine ions in acid solution may be expressed as follows:

$$2CrO_4^{=} + 6I^{-} + 16H^{+} = 2Cr^{+++} + 8H_2O + 3I_2$$

This equation shows that 1 atom of chromium is equivalent to 3 atoms of iodine or 1 cc. of normal sodium thiosulfate solution is equivalent to 0.01733 g. of Cr. By multiplying this last value by the value expressing the relation of the sodium thiosulfate solution to the normal solution, *i.e.*, its normality, the value of 1 cc. of the thiosulfate solution in terms of chromium is obtained.

Preparation and Standardization of Permanganate and Ferrous Sulfate Solutions.—A suitable solution of permanganate may be prepared by dissolving about 16 g. of potassium permanganate in 5 liters of water. The preparation and standardization of such a solution was discussed under Manganese, p. 204.

To prepare a ferrous sulfate solution of corresponding concen-

[1] The starch solution is prepared by dissolving 0.5 g. of soluble starch in 25 cc. of hot water. It is ready for use as soon as it cools.

tration, dissolve 60 g. of pure ferrous sulfate crystals, $FeSO_4.7H_2O$ in water, add 100 cc. of concentrated sulfuric acid, and dilute to 2 liters.

The ferrous sulfate solution is not very stable but gradually weakens owing to the slow oxidation of the ferrous ions. For this reason, its strength compared with that of the permanganate must be determined on the same day that the analysis for chromium is made. Measure out a portion of the solution by means of a pipette, dilute to 100 cc. and titrate with permanganate. Use the same quantity of ferrous sulfate as in the analysis for chromium. The quantity chosen must be sufficient to react with all the chromium present so that an excess remains to be titrated with permanganate. Then, by subtracting the volume of permanganate used in titrating the excess of ferrous sulfate in an analysis, from the volume of permanganate which has been found to be required for all of the ferrous sulfate used, the difference gives the volume of permanganate which is equivalent to the chromium in the sample.

The reaction between the chromate and ferrous ions may be expressed as follows:

$$CrO_4^{--} + 3Fe^{++} + 8H^+ = Cr^{+++} + 3Fe^{+++} + 4H_2O$$

The reaction between ferrous and permanganate ions is:

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O$$

Since the change in valence of the chromium is three, it is clear that 1 cc. of normal permanganate is equivalent to $\frac{Cr}{3000} =$ 0.01733 g. Cr, as in the titration with sodium thiosulfate.

In the standardization of the permanganate against sodium oxalate the reaction is

$$5C_2O_4^{--} + 2MnO_4^- + 16H^+ = 10CO_2 + 2Mn^{++} + 8H_2O$$

If n cc. of permanganate are used in titrating e g. of sodium oxalate then the normality of the permanganate solution is

$$\frac{e}{n \cdot \frac{Na_2C_2O_4}{2000}} = \frac{e}{0.067n}$$

and the value of 1 cc. permanganate in terms of chromium is

$$\frac{0.01733 \times e}{0.067n} = \frac{e}{n} \cdot 0.2587 \text{ g. Cr}$$

Mercurous Nitrate Solution.—Pulverize 100 g. of pure mercurous nitrate and shake it with water in a glass-stoppered liter bottle.

To prevent oxidation, add a little pure mercury. The mercurous nitrate is hydrolyzed to some extent so that the solution always contains free acid and some basic mercurous nitrate remains at the bottom of the bottle.

Procedure.—Of pig iron and steel with low chromium content take 10 to 15 g., of richer materials 4 to 5 g. Dissolve the sample in a porcelain dish with dilute nitric acid[1] (sp. gr. 1.2), evaporate to dryness, destroy the nitrates, take up with hydrochloric acid and remove the silica as in Method 1B, p. 173.[2]

The silica frequently holds back a little chromium. After volatilizing the silica with sulfuric and hydrofluoric acids, therefore, test for chromium. Mix it in the platinum crucible with a little magnesia-sodium carbonate mixture and heat strongly for half an hour. Extract the product obtained with hot water to dissolve the sodium chromate. Filter off the residue and acidify the filtrate with hydrochloric acid. Add about 0.25 g. of potassium iodide and titrate any liberated iodine with the tenth-normal sodium thiosulfate solution. Instead of titrating the sodium chromate, it can be treated as described on p. 293 and the chromium weighed as oxide.

Evaporate the filtrate from the silica, and shake with ether as described on p. 185.

Precipitate the copper as sulfide from the hydrochloric acid solution and in the filtrate carry out the treatment with caustic soda and sodium peroxide as described on p. 189.

Treat the fusion in the platinum dish with water; all the chromium goes into solution as sodium chromate and part of the

[1] Some samples of materials rich in chromium do not dissolve readily in nitric acid; in such cases concentrated hydrochloric acid, without the use of an oxidizing agent, may be used. If this dissolves the sample, evaporate to dryness, remove the silica by Method 1A, p. 169, oxidize the iron with nitric acid and prepare for the ether separation in the usual way.

[2] To hasten the process, the procedure described on p. 200, may be used

manganese dissolves as sodium manganate, imparting a green color to the solution. In case the excess of sodium peroxide used is insufficient to convert the manganese to manganese dioxide on boiling the solution,[1] add one or two knife-bladefuls more of this reagent, stir well and cover with a watch-glass.

Transfer the solution to a 300 cc. beaker, dilute with water to about 200 cc., and allow the precipitate to settle while heating on the water bath. Cool, filter the clear solution, which is colored more or less yellow according to the quantity of chromium present, and wash the precipitate, which contains all the manganese, nickel, cobalt and residual iron, with hot water until the washings are no longer alkaline to litmus. The precipitate may be used for the determination of manganese, nickel and cobalt. The aqueous solution may contain besides sodium chromate, some sodium phosphate and sodium vanadate according to the extent that these elements are present in the original material. If vanadate is present it interferes somewhat with the iodometric determination of the chromium, as it is reduced slowly by means of hydriodic acid. It is hard to get a good end point with sodium thiosulfate and the results for chromium are too high.

It is also claimed that vanadic acid influences the volumetric estimation of the chromium when ferrous sulfate and potassium permanganate are used in the titration, though Campagne has shown that good results can be obtained in the presence of vanadium.

It is safer to remove the vanadium before attempting to titrate the chromium.

By treating the aqueous solution with mercurous nitrate solution, mercurous chromate, phosphate and vanadate are precipitated.

To recover the chromium in it, this precipitate must be filtered off, the filter and precipitate ignited, the mercury volatilized and the residue subjected to a suitable fusion process (*cf.* pp. 189, 294, 298).

If the chromate solution shows only a slight pale yellow color, the whole of it may be taken for the chromium titration. If much chromium is present, as shown by a deep yellow color,

[1] In such cases purple permanganate ions are usually present.

transfer the solution to a 500 cc. calibrated flask and take an aliquot part, *e.g.*, 50 cc. for the titration.

It is not advisable to attempt to titrate more than 0.1 g. of chromium or the solutions, toward the end of the titration, will become so green with chromic ions that it is difficult to detect the correct end point. This is true whether the determination is carried out by the iodometric method or by means of ferrous sulfate and permanganate. When strongly colored, it is necessary to dilute largely before titrating.

α. Iodometric Determination of Chromium.—Before acidifying the alkaline chromate solution, it is necessary to decompose the excess sodium peroxide by boiling. If any of it is left undecomposed, hydrogen peroxide is formed on making the solution acid. This may unite with the chromic acid to form blue perchromic acid which is not very stable and decomposes readily into chromic salt. Some of the chromium, therefore, is likely to miss the titration if any hydrogen peroxide is formed. After decomposing all the excess of sodium peroxide, transfer the solution to a 600 cc. Erlenmeyer flask, acidify the cold solution with hydrochloric acid, and add 1 g. of pure potassium iodide, which must be free from iodate,[1] to about 200 to 300 cc. and titrate with thiosulfate solution until the iodine color fades to a pale yellow, then add 2 cc. of starch solution and titrate till the blue color just disappears.

Computation.—If in the analysis of s g. of material, n cc. of f-normal thiosulfate solution were used, including that required for titrating the chromium found in the residue from the silica, then

$$\text{per cent. Cr} = 1.733\, f\, \frac{n}{s}$$

The value f, as described on p. 289, is obtained by dividing the value of 1 cc. of the sodium thiosulfate solution in terms of the substance against which it is standardized by the value of 1 cc. of a *normal* solution of sodium thiosulfate in terms of the same substance.

(β) Titration with Ferrous Sulfate and Permanganate.—To the chromate solution freed from excess of sodium peroxide, as in

[1] *cf.* pp. 206, 287.

Method α, add dilute sulfuric acid (1:10) in moderate excess and dilute the solution to about 300 cc. Add, by means of a pipette, 25 or 50 cc. of ferrous sulfate solution. Enough ferrous sulfate must be used to reduce all of the yellow chromate ion to green chromic ion. If more than 50 cc. are required to accomplish this reduction, it is advisable to work with a smaller sample, obtained by taking an aliquot part of the solution as already described.

Then, without allowing the solution to stand very long, titrate slowly with permanganate. Titrate a fresh portion of the ferrous sulfate solution alone against the permanganate, using the same pipette that was used in the analysis.

Computation.—If a cc. of f-normal permanganate were used in titrating a pipetteful of ferrous sulfate and b cc. of permanganate were used in the analysis of s g. of material, then

$$\text{per cent. Cr} = \frac{1.733 f (a - b)}{s}$$

or, if T represents the value of 1 cc. permanganate in terms of chromium (p. 290).

$$\text{per cent. Cr} = \frac{100 T (a - b)}{s}$$

(γ) *Precipitation with Mercurous Nitrate Solution.*—For the chromium determination use all or a part of the filtrate from the fusion with sodium peroxide (p. 189) according to the amount of chromium present.

Transfer the solution to a 300–400-cc. beaker and cautiously neutralize it with dilute nitric acid. Stop adding the acid as soon as a piece of litmus paper in the solution assumes a wine-red color. Then add mercurous nitrate solution, cover the beaker with a watch-glass and boil the solution a short time. Allow the precipitate, which is gray or grayish green when thrown down from faintly alkaline solutions, and red (or yellow) when thrown down from faintly acid solutions, to settle to the bottom of the beaker and test with more mercurous nitrate solution to see if the precipitation is complete.

The mercurous nitrate solution is always slightly acid as a result of the hydrolysis, so that, when much of the reagent is

added, the solution may become so acid that the precipitation of the chromic acid is incomplete. In such cases a few drops of ammonia may be added and the solution again heated. This must be done with caution, for an excess of ammonia will cause the formation of soluble ammonium chromate and the precipitation of the chromic acid will be incomplete. After the precipitate has settled, test again with a little more mercurous nitrate solution. Filter off the precipitate through an ashless filter paper and wash it first with pure water and finally with very dilute mercurous nitrate solution (25 cc. of the reagent diluted to 500 cc.). If it is intended to purify the precipitate, it is not necessary to wash it entirely free from alkali salts.

Ignite the filter together with the precipitate in an open platinum crucible under a good hood (on account of the poisonous vapors) and finally heat strongly. Sometimes the ignited chromic oxide, Cr_2O_3, which is formed by the ignition of the mercurous chromate, is pure enough to weigh. This is seldom the case in the analysis of steel. Of the elements likely to be present in steel, mercurous nitrate solution will precipitate the phosphorus as phosphate, the vanadium as vanadate, the tungsten as tungstate, and the molybdenum as molybdate. Of these elements, phosphorus and vanadium are the only ones that need be considered. The tungstic acid will be precipitated practically completely with the silica and will be left as a yellow residue after the volatilization of the silicon as fluoride. Molybdenum follows the iron in the ether separation so that very little of it can be present at this stage in the analysis. The method of purifying the precipitate, however, would serve equally well for separating chromium from phosphorus, vanadium, tungsten and molybdenum.

Purification of the Impure Chromic Oxide.—The purification process to be described depends upon the fact that it is possible by means of an alkaline reducing fusion to keep the chromium as insoluble chromic oxide while converting the impurities into soluble alkali salts. A suitable flux is prepared by mixing 4 parts of pure double carbonate of sodium and potassium with 1 part of pure potassium acid tartrate. Instead of the double carbonate, sodium carbonate may be used. (Another suitable flux may be prepared with sodium carbonate and sodium acetate.)

Commercial potassium acid tartrate (cream of tartar) is likely to contain a little calcium sulfate. In case pure potassium acid tartrate is not at hand, it may be prepared by adding a filtered solution of 150 g. of tartaric acid to an aqueous solution of 56 g. of pure caustic potash. Cool the solution, filter off the crystals with the aid of suction, and dry them at 105° in the hot closet.

Mix the impure chromic oxide in the platinum crucible with 8 to 10 times as much of the carbonate-tartrate mixture and heat with a moderate flame. The potassium acid tartrate soon begins to decompose. Raise the cover of the crucible and watch the carbonization and fusing together of the contents. The carbon that is deposited from the tartrate gradually oxidizes to carbonic oxide gas in the fusion mixture. As soon as nearly all of the free carbon is gone, stop fusing.

Special attention must be paid to the proper timing of the fusion. If it is continued too long, some of the chromic oxide will be oxidized to chromate, imparting a yellow color to the fusion. If the fusion is not continued long enough, some of the impurities may not be converted to soluble alkali salts.

If considerable chromic oxide is to be purified, it is rather better to fuse it first with pure sodium carbonate and then reduce the chromate by the addition of potassium acid tartrate finishing the treatment as described.

After cooling, place the crucible in a small beaker and warm the melt with a little water. When all of the alkali salts have dissolved, remove the crucible, washing it well with hot water, and filter the solution through an ashless filter. Chromic oxide, mixed with some charcoal, remains behind upon the filter. Wash the filter and precipitate thoroughly with hot water and finally with a few drops of very dilute nitric acid, to make sure that all the alkali salts are dissolved. Ignite the precipitate in a platinum crucible and weigh the green chromic oxide, Cr_2O_3.

If desired, the purity of the chromic oxide may be verified by fusing it with magnesia-sodium carbonate mixture (p. 290) dissolving the sodium chromate in water and titrating the chromate in acid solution by either Method α or Method β.

The filtrate from the fusion for the purification of the chromic

oxide may be used for the determination of phosphorus or of vanadium.

Computation.—If p g. of chromic oxide were obtained in the analysis of a sample weighing s g. then

$$\text{per cent. Cr} = \frac{2\text{Cr} \times p \times 100}{\text{Cr}_2\text{O}_3 \times s} = \frac{68.42p}{s}$$

The chromium carried down by the silica must also be taken into consideration (p. 290).

(b) Rapid Methods for the Determination of Chromium

In a busy chemical laboratory it is often necessary to determine the chromium content of a sample of iron or steel very quickly. Many rapid methods have been proposed and most of them, if the analyst is familiar with the proper technique, give results which are nearly, if not quite, as accurate as those obtained by one of the longer methods. Two such methods will be described.

(α) Barba's Method[1]

Principle.—The chromium is oxidized to chromic acid in sulfuric acid solution by means of potassium permanganate, the excess of the latter is reduced by making the solution ammoniacal and boiling, and the chromium is determined by the ferrous sulfate-permanganate method.

Procedure.—Dissolve 1.25 g. of steel in 20 cc. of dilute sulfuric acid (1:5). If an insoluble residue remains, test it for chromium as described on p. 290. Add concentrated nitric acid, drop by drop, to the hot solution until the iron is all oxidized to the ferric condition. About 2 cc. are sufficient. Boil to remove nitrous fumes and add from a pipette 5 cc. of concentrated potassium permanganate solution (6 g. $KMnO_4$:100 cc. water). Boil the solution briskly for 15 to 20 min., then wash down the sides of the beaker, and add 25 cc. of strong ammonia (sp. gr. 0.90) pouring it down the sides. Stir well and replace the beaker on a cooler part of the hot plate to avoid "bumping." Stir occasionally and digest about 15 min., or until the permanganate is all

[1] The Iron Age, **52**, 153.

decomposed. Add cautiously 20 cc. of sulfuric acid (1:1) and bring to a gentle boil. Then cool the solution to room temperature and transfer to a 250 cc. flask. Make up to the mark and mix thoroughly by pouring the solution back and forth into a beaker several times. Filter through a dry filter into a dry beaker, rejecting the first few cc., and use an aliquot part of the filtrate, usually 200 cc. (= 1 g. of the steel).

Determine the chromium by adding ferrous sulfate and titrating the excess with permanganate (*cf.* p. 292).

(β) Bismuthate Method

Principle.—In *cold* solutions containing 20–40 per cent. of concentrated nitric acid, manganese can be oxidized from the bivalent to heptavalent condition. Chromium is oxidized so slowly under such conditions that, if the solution is promptly filtered, the manganese may be titrated by the ferrous sulfate-permanganate method (*cf.* p. 216). In *hot* solutions permanganic acid in contact with sodium bismuthate is decomposed, usually forming manganese dioxide, and chromium is oxidized from the trivalent to hexavalent condition. In hot solutions, therefore, chromium can be determined by the ferrous sulfate-permanganate method, without the manganese doing any harm. Some chemists, in fact, have intentionally added manganese to the solution because manganese dioxide will oxidize chromium.

Procedure.—Dissolve 3 g. of steel, or less if the sample contains more than 1 per cent. Cr, in a 250 cc. Erlenmeyer flask with 50 cc. of nitric acid (sp. gr. 1.13 = 25 per cent. conc. acid by vol.). If there is any carbonaceous residue, as in the analysis of cast irons, it should be filtered off and examined for chromium by fusion with an alkaline oxidizing flux (*cf.* p. 290). If the metal is difficultly soluble in nitric acid, it is sometimes necessary to add sulfuric acid to facilitate solution.

When the sample is all dissolved, cool the solution slightly (65° to 75°) and add 2 g. of sodium bismuthate. Agitate a few minutes and then wash down the sides of the flask with a little water. Heat to boiling and boil gently until the permanganate formed from the manganese in the steel is all decomposed as shown by the color; this usually requires about 15 min.

Add 50 cc. of three per cent. nitric acid (3 cc. HNO_3, sp. gr. 1.42 : 100 cc. water) and filter off any precipitated manganese dioxide or undissolved sodium bismuthate on an asbestos filter. Wash the residue 3 times with 50 cc. portions of the dilute nitric acid. Cool to room temperature by running tap water over the flask and dilute with distilled water to 500 cc. Add a measured excess of ferrous sulfate solution and titrate the excess with standard permanganate as described on p. 293.

(c) Determination of Chromium by the Fusion Method

Principle.—The sample is converted into oxide and the chromic oxide is converted to chromate by fusing with sodium peroxide in a nickel or iron crucible. The method is suitable for chrome-steel, chrome-nickel steel, chrome-tungsten steel and chrome-vanadium steel; steels with low chromium content are analyzed preferably by one of the methods already described, using a larger sample.

Procedure.—Treat 2 g. of the metal in a small porcelain evaporating dish with six-normal nitric acid (sp. gr. 1.2) evaporate the solution to dryness, and heat the residue until the nitrates are decomposed, keeping the dish covered with a watch glass to prevent loss by spattering. During the heating, the oxides are dislodged, for the most part, from the sides of the dish. Transfer the loose particles to an agate mortar, mix them with sodium peroxide (about 16 g. is used in an analysis) and transfer the mixture to a well-scoured nickel or iron crucible.[1] Carefully scrape off with a spatula as much as possible of the oxide from the porcelain dish, mix it with sodium peroxide and add the mixture to the crucible. Next place a little sodium peroxide in the dish, rub the dish with it and transfer to the crucible. Finally add a little caustic soda solution to the dish, heat it nearly to boiling and rinse the solution into a beaker, setting it aside for the time being.

Cover the crucible and heat it with a small flame until the mass melts, then raise the temperature and heat to dull redness for about 15 min. Allow the crucible to cool, place it in a beaker, add

[1] A new iron crucible is usually covered with some sort of varnish. To remove it, heat the crucible to redness over a Méker burner or a blast lamp and plunge the red hot crucible into water.

hot water, and cover the beaker with a watch-glass. The mass dissolves quickly with decomposition of most of the excess of peroxide. Add the reserved alkali solution with which the evaporating dish was washed, remove the crucible, washing it thoroughly, and allow the beaker and its contents to stand an hour or two on the steam bath. If the solution should not be yellow but green in color, owing to the presence of manganate, add a little sodium peroxide and stir; this serves to reduce the manganate to manganese dioxide. Dilute the solution to 200 cc., allow it to cool and, when well settled, decant the supernatant liquid through a filter, without disturbing the residue. Cover the residue with hot water and allow it to settle again. Then filter as before, catching the filtrate in a fresh beaker so that if any of it runs through turbid it will not be necessary to refilter the entire filtrate. Transfer the residue to the filter and wash it with hot water until the washings are neutral to red litmus paper.

A little chromium is likely to remain with the iron in an insoluble condition such that it is impossible to remove it by washing. To recover this chromium, ignite the precipitate and filter and repeat the fusion with sodium peroxide in exactly the same manner as before, finally combining the aqueous extract of the fusion with that first obtained.

Boil the solution until all the excess of sodium peroxide is destroyed, cool to room temperature and dilute up to the mark in a 500 cc. calibrated flask. Use an aliquot part, usually one-fifth, for the determination of the chromium according to p. 292.

If preferred, the aqueous, alkaline solution of sodium chromate may be used for the gravimetric determination of chromium according to p. 293. In that case, treat the impure chromic oxide with sulfuric and hydrofluoric acids and heat to expel any silica, before fusing it with the alkaline reducing flux.

2. DETERMINATION OF CHROMIUM IN MATERIALS INSOLUBLE IN ACID

The method is applicable to the analysis of ferro-chrome, chrome-tungsten steel, etc.

Procedure.—Intimately mix from 0.5 to 2 g. of the pulverized sample with 10 times as much of the Rothe fusion mixture (p. 178), transfer the mixture to a platinum crucible, and heat half an hour over a Tirrill burner and the same length of time

over a large Méker burner, or over a blast lamp. Transfer as much as possible of the ignited product to an agate mortar, moisten it with a little water and crush it carefully to a paste. Rinse the paste into a beaker and heat on the steam bath to extract the soluble chromate. Allow the residue to settle, decant the solution through a filter, and wash the residue by decantation and then thoroughly on the filter, with hot water. Ignite the filter and residue in the platinum crucible and fuse it with about 4 times as much sodium carbonate as the original sample weighed. After cooling the crucible, extract the soluble sodium salts and repeat the fusion with sodium carbonate in order to remove the last traces of chromium. If the material was sufficiently fine, the quantity of chromium left in the residue after the third fusion is perfectly negligible.

The residue may be used for the determination of iron, manganese, or nickel.

Combine all the aqueous extracts and dilute to 500 or 1000 cc. in a calibrated flask. Take an aliquot part for the chromium determination, according to p. 292, bearing in mind that the solution may contain vanadate or tungstate of sodium.

Test Analysis. 1. *Separation of Chromium and Iron by the Ether Method.*—Ten cubic centimeters of a solution of chromic chloride was analyzed by the permanganate process and found equivalent to 53.5 cc. of permanganate (= 0.1083 g. Cr).

In duplicate experiments, 10 cc. of the chromic chloride solution were mixed with 50 cc. of pure ferric chloride solution (= 4.4 g. Fe), the iron removed by the ether method and the chromium determined by Method 1B, p. 292. In one experiment 53.5 cc. of permanganate were used and in the other 53.3 corresponding to 0.1083 and 0.1079 g. Cr; this shows that the separation is accurate within the usual limits of error.

Two experiments were carried out with respectively 5 and 10 cc. of another chromic chloride solution (= 0.0031 and 0.0062 g. Cr) in the presence of ferric chloride solution corresponding to 3.2 g. Fe. In this case the analysis was finished by titration with sodium thiosulfate solution and the values agreed perfectly to the two significant figures given above, showing that with low chromium the process gives results agreeing within 0.0001 g. of chromium.

2. *Analysis of Various Chrome Steels.*—A sample of chrome steel weighing 6.000 g. was analyzed by Method 1*a* and one-fifth of the solution was taken for the final determination. Volumetrically, by the permanganate method, the value 4.07 per cent. Cr was obtained which agreed well with 4.05 per cent. Cr, the value obtained gravimetrically.

A sample of nickel-chrome steel, weighing 6 g., was analyzed by the sodium thiosulfate method, using two-fifths of the original solution, and the value 0.22 per cent. Cr was obtained. Another test was carried out with a 6-g. portion of the steel and using the entire solution for the final titration. In this case the value 0.23 per cent. Cr was obtained.

A sample of chrome-tungsten steel with 6 per cent. tungsten, analyzed by Method *a*, gave 5.82 per cent. Cr and by Method *b*, 5.84 per cent. Cr. In this case 0.04 per cent. Cr was recovered from the silica.

A sample of chrome-tungsten steel with 4 per cent. W, analyzed by Method *a*, showed 10.22 per cent. Cr and by Method *b*, 10.36 per cent. Cr. In this case the chromium from the silica in Method *a* in one case amounted to 1.06 per cent.

A sample of ferro-chrome was analyzed by Method 2. One gram of the substance was weighed out and one-tenth of the solution taken for the final titration with sodium thiosulfate. In duplicate determinations the values 60.8 and 60.7 per cent. Cr were obtained.

3. *Purification of Chromic Oxide Precipitates.*—Ten cubic centimeters of tungstate solution (0.2724 g. WO_3) were mixed with 10 cc. of chromate solution (0.0250 g. Cr_2O_3) and the solution precipitated with mercurous nitrate. After purification with the potassium acid tartrate mixture, the Cr_2O_3 obtained weighed 0.0252 g.

A similar experiment with vanadate solution (0.153 g. V_2O_3) and chromate solution (0.0500 g. Cr_2O_3) gave 0.0505 g. of purified Cr_2O_3.

Accuracy of the Results and Permissible Variations.—With chromium content of less than 0.5 per cent. duplicate determinations should agree within 0.005 per cent. and with 10 per cent. Cr, or more, the values should agree within 0.1 per cent. The values should also closely approximate the truth.

CHAPTER XI

ALUMINIUM

In the manufacture of ingot iron and mild steel, aluminium is often added for the purpose of deoxidizing the molten metal. Aluminium is present in iron, therefore, chiefly in the form of its oxide. If more aluminium is added than is necessary to combine with all the oxygen, then some of it will remain in solid solution with iron. At the present time there is no absolutely dependable analytical test to determine whether the small quantity of aluminium usually found is present as oxide or as metal. Certain special alloys, *e.g.*, aluminium steel, are certain to contain metallic aluminium.

Principle.—Aluminium, like manganese, chromium, nickel, etc., can be separated from iron by the Rothe method of shaking the chlorides in hydrochloric acid solution with ether. In determining the aluminium by precipitation as aluminium hydroxide from dilute acetic acid solution, it is necessary to bear in mind that the phosphorus from the steel is likely to be precipitated at the same time as aluminium phosphate;[1] for this reason it is advisable to precipitate the aluminium intentionally as aluminium phosphate.

Procedure.—Weigh from 5 to 10 g. of steel into a porcelain dish and dissolve it in 60 to 120 cc. of concentrated hydrochloric acid. Evaporate the solution to dryness and remove the silica according to Method 1A,[2] p. 169. Avoid dehydrating the silica at too high a temperature on account of the danger of volatilizing aluminium chloride; there will be no loss in a hot closet at 135°. The deposited silica is likely to retain a little aluminium.[3] After treating the silica with hydrofluoric and sulfuric acids, therefore, fuse the residue with a little sodium carbonate and determine the

[1] When steel is dissolved in hydrochloric acid, some of the phosphorus is evolved as phosphine.

[2] Or by method 1B, p. 173; *cf. d*, p. 200.

[3] If the residue contains much aluminium this indicates that it was originally present as oxide.

aluminium as hydroxide or as phosphate as described for the main determination.

Concentrate the filtrate from the silica by evaporating until a crust of crystals begins to separate on the edges of the solution; then add, to the hot solution, dilute nitric acid (sp. gr. 1.2) in small quantities and cover the dish with a watch glass. When the oxidation of the iron is complete, which is recognized by the fact that no more oxides of nitrogen are evolved and the solution in the dish becomes transparent,[1] remove the watch glass and evaporate the solution to dryness. To remove any remaining nitric acid, take up the residue with concentrated hydrochloric acid and evaporate to the consistency of sirup. Shake the solution of the chlorides with ether in the usual manner (*cf.* p. 185).

Evaporate the aqueous chloride solution, which is nearly free from iron, to remove the ether and dissolve the residue in a little hydrochloric acid. Dilute the solution until it contains about 25 cc. of water for each cc. of hydrochloric acid (sp. gr. 1.12) present, precipitate the copper by adding a little hydrogen sulfide water to the hot solution and filter off the copper sulfide.

Add a few cc. of dilute sulfuric acid to the filtrate and evaporate the solution in a porcelain dish until fumes of sulfuric acid are evolved; it is necessary to heat over a free flame toward the last. The reason for transforming the chlorides into sulfates is because the aluminium precipitate filters better when deposited from a sulfate solution. Dissolve the residue of sulfates in water, heating till all is dissolved, and dilute to about 100 cc. in a 200- to 250-cc. beaker. Add ammonia until the solution is alkaline to litmus paper and at once redissolve the aluminium hydroxide with as little dilute sulfuric acid as possible. A little brown oxide of manganese usually remains undissolved; take this up by adding about 1 cc. of sulfurous acid. To the slightly acid solution, add 2 or 3 cc. of neutral ammonium acetate solution (100 g. in 500 cc. of water); the solution should still have a slightly acid reaction.

Heat the solution to boiling, which causes all the aluminium to precipitate together with some impurity. After allowing the

[1] When the nitric acid is first added, a dark brown compound with NO and ferrous salt is formed. This disappears when no more ferrous salt is present.

precipitate to settle, filter and wash the precipitate with water containing a little ammonium acetate. Finally rinse back the precipitate into the original beaker and dissolve it in as little sulfuric acid as possible, heating on the water bath to aid the solution. Repeat the precipitation with ammonium acetate and filter through the same filter, washing as before.

The filtrate now contains all the nickel and manganese and the precipitate consists chiefly of aluminium hydroxide and phosphate. Rinse the precipitate back into the beaker, dissolve it once more in dilute sulfuric acid, avoiding an excess, add 1 or 2 cc. of ammonium phosphate solution (100 g. in 500 cc. of water) and reprecipitate the aluminium by adding a very slight excess of ammonia to the boiling hot solution.

After the precipitation is complete, acidify slightly with acetic acid, heat to boiling, filter and wash the precipitate with hot water containing a little ammonium acetate. Ignite and weigh as $AlPO_4$.

When perfectly pure, the aluminium phosphate is white. If small amounts of chromium are present in the original metal, it is precipitated as chromic phosphate with the aluminium phosphate and the precipitate has a grayish or green tint. In such cases, fuse the ignited precipitate with a little sodium carbonate and determine the chromic acid by treating the acid extract of the melt with potassium iodide and titrating the iodine set free with standard thiosulfate solution (*cf.* p. 292). Compute the quantity of chromic phosphate corresponding to this titration and subtract it from the weight of the phosphate precipitate previously obtained.

When the Rothe separation is successfully accomplished, not more than 1 or 2 mg. of iron should follow the aluminium into the aqueous layer obtained in the treatment with ether. In such cases the aluminium precipitate is not contaminated with iron, which is in the ferrous condition owing to the addition of sulfurous acid. If, however, the first precipitation of hydroxides obtained in the above procedure is plainly contaminated with iron, it is advisable to evaporate the sulfuric acid solution to dryness in a platinum dish, heat until the free sulfuric acid is all expelled, and fuse with a little caustic soda and sodium peroxide, as described under Manganese, p. 189. Neutralize the aqueous extract of the melt with sulfuric acid, remove the sodium

salts by precipitating the aluminium twice with ammonia, and finally precipitate the aluminium phosphate as described above.

Computation.—If a sample of steel weighing s g. gives p. g. of aluminium phosphate, then

$$\text{Per cent. Al} = \frac{p \times \text{Al} \times 100}{\text{AlPO}_4 \times s} = \frac{22.19p}{s}$$

Test Analysis. 1. *Experiments with Aluminium Chloride Solution.*—Twenty cubic centimeters of an aluminium chloride solution free from phosphoric acid gave, in two experiments by precipitation with ammonium acetate and weighing as Al_2O_3, the values 0.0464 and 0.0465 g. Al.

The same quantities of solution analyzed by precipitation as $AlPO_4$ gave the values 0.0475 and 0.0477 g. Al.

In two other experiments, in which ferric chloride equivalent to 5 g. of metallic iron was added in each case, the values 0.0491 and 0.0475 g. Al were obtained.

2. *Analysis of Aluminium Steel. Sample* 1.—Duplicate determinations in 5-g. samples gave the values 0.23 and 0.25 per cent Al. The silica precipitate contained no aluminium.

Sample 2.—(*a*) In the analysis of a sample weighing 5 g., a precipitate of aluminium phosphate weighing 0.0687 g. was obtained in the main analysis. This precipitate was contaminated with chromium and the subsequent titration with sodium thiosulfate showed 0.0036 g. of $CrPO_4$. Subtracting this from the original weight of the phosphate precipitate, the value 0.292 per cent. Al was obtained.

The silica precipitate was tested for aluminium and additional aluminium amounting to 0.033 per cent. obtained, making the total Al content = 0.33 per cent.

(*b*) A duplicate determination with similar results gave 0.34 per cent. Al.

Accuracy of Aluminium Values and Permissible Deviations

The values reported in samples containing up to 1 per cent. Al should be accurate to within 0.05 per cent., provided a careful blank is made with the same quantities of reagents as used in a regular analysis.

CHAPTER XII

TITANIUM

Pig iron prepared from ores containing titanium often contains small quantities of this element. Moreover, titanium, like aluminium, is used as a deoxidizing agent and in some cases a little of the titanium gets into the metal in this way. Usually, however, the quantity of titanium used is regulated so that all of it goes into the slag.

Ferro-titanium and manganese-titanium are the principle alloys of titanium that are used in metallurgical operations.

1. DETERMINATION OF TITANIUM IN MATERIALS SOLUBLE IN ACID

Principle.—Titanium may be freed from the greater part of the iron by means of the Rothe ether separation (p. 185). After the ether treatment, the solution contains manganese, nickel, chromium, possibly some other metals and phosphoric acid besides the titanium and a little of the iron.

The titanium may be precipitated from such a solution by boiling an acetic acid solution[1] containing ammonium acetate and something to keep iron in the ferrous condition, but in most cases it is necessary to purify the titanium dioxide that is obtained by such a procedure. The weight of the impurities is deducted from the weight of impure titanium dioxide. The titanium may also be determined colorimetrically, or, if the titanium content is not too low, it may be determined by a volumetric process.[2]

Apparatus and Solutions Required.—

For the Ether Treatment:

Rothe shaking funnel, *Fig.* 120, *p.* 184.

Hydrochloric acid (*sp. gr.* 1.10).

Ether-hydrochloric Acid Solutions.—One solution is made by adding ether to concentrated hydrochloric acid (sp. gr. 1.2) until a layer of ether is formed after shaking, and the other solution is prepared from dilute hydrochloric acid (sp. gr. 1.10), in the same way.

[1] *cf.* Barnebey and Isham, J. Am. Chem. Soc., **32**, 957 (1910).

[2] *cf.* Hinrichsen, Chem.-Ztg., **31**, 738 (1907).

FOR TITRATING THE TITANIUM:

Ferric Chloride Solution.—Moisten 27 g. of pure ferric chloride crystals ($FeCl_3\ 6H_2O$) with 10 cc. of hydrochloric acid (sp. gr. 1.12), dissolve by warming with water and dilute the solution to 1 liter. The hydrochloric acid is necessary to prevent hydrolysis of the ferric chloride, whereby a basic chloride is precipitated which makes the solution unfit for use.

The ferric chloride solution may be standardized against tenth-normal sodium thiosulfate solution (*cf.* p. 287) or against tenth-normal permanganate (p. 204).

To standardize against sodium thiosulfate solution, measure out by means of a burette or pipette 35–50 cc. of the ferric chloride solution into a 200-cc. Erlenmeyer flask and concentrate to about 15 cc. Add 2 cc. of dilute hydrochloric acid (sp. gr. 1.12), and a solution of 3 g. potassium iodide dissolved in a little water; the potassium iodide must be free from iodate and its aqueous solution should remain colorless upon the addition of a little hydrochloric acid.[1] By means of hydriodic acid, ferric ions are reduced to ferrous ions and iodine is set free;

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$$

The iodine is titrated with tenth-normal sodium thiosulfate solution, adding starch solution toward the last. To reduce traces of ferric chloride that still remain in the solution, heat to 50°, or 60° at the most, cool to room temperature by running cold water upon the flask, add a little more starch solution and finish the titration with sodium thiosulfate.

To standardize against potassium permanganate, the Zimmermann-Reinhardt method[2] is suitable. Measure out, by means of pipette or burette, 25–50 cc. of the ferric chloride solution into a small beaker, add 10 cc. of hydrochloric acid (sp. gr. 1.12), and heat the solution nearly to boiling. Place the beaker on a piece of white filter paper and add stannous chloride solution (50 g. stannous chloride crystals, and 100 cc. concentrated hydrochloric acid; heat till dissolved and dilute with water to 1 liter), drop by drop, until the yellow color of ferric chloride disappears from the hot solution. Take pains not to add a single drop of the stannous chloride in excess of the quantity necessary to render the solu-

[1] If iodine is liberated, an allowance for this must be made in the analysis.

[2] Zimmermann, Ber., **14**, 779 (1881); Reinhardt, Chem.-Ztg., **13**, 323 (1884).

tion colorless. If more is used by accident, add a few drops of potassium permanganate solution to oxidize the excess stannous chloride and enough of the iron to give a slight yellow color (ferric chloride) to the solution and repeat the reduction with stannous chloride. Cool the solution to room temperature and quickly add 10 cc. of mercuric chloride solution (50 g. to 1000 cc. water). Allow the solution to stand 5 min. to complete the reaction between the excess stannous chloride and the mercuric chloride, whereby a silky precipitate of mercurous chloride is formed, then dilute to about 400 cc. and add 20 cc. of acid manganese sulfate solution (prepared by dissolving 67 g. of manganous sulfate crystals, $MnSO_4.4H_2O$, in 500 cc. water, adding 138 cc. of phosphoric acid (sp. gr. 1.7), and 130 cc. of sulfuric acid (sp. gr. 1.84), and diluting to 1 liter). After the addition of the manganese sulfate solution, titrate the ferrous solution slowly with tenth-normal permanganate. At no time should the solution of permanganate be added faster than the drops can be counted and it is important at the start and finish not to add a drop of permanganate until the color produced by the previous drop has disappeared entirely.

This method of standardization gives good results with a little practice. It is necessary to add the manganese sulfate solution as otherwise the dilute hydrochloric acid is oxidized by the permanganate in the presence of ferrous salt, and the results of the standardization will be too low on account of the use of too much permanganate. It is important to follow the directions very carefully.

Procedure.—Weigh out 10–15 g. of the iron or steel into a porcelain dish, and dissolve it in nitric acid (sp. gr. 1.18), using about 12 cc. of acid for each gram of sample. Evaporate the solution to dryness, take up in hydrochloric acid and remove the silica in the usual way (p. 173). The silica carries down a little titanium dioxide with it. After volatilizing the silicon as tetrafluoride, therefore, fuse the residue with sodium carbonate, dissolve the melt in hydrochloric acid (sp. gr. 1.12) and add the solution to the filtrate from the silica.

Concentrate the solution and remove the ferric chloride as completely as possible by the ether method (p. 185). The presence of titanium is often betrayed by the hydrochloric acid solu-

tion becoming somewhat turbid after the first shaking with ether and more turbid after the second shaking, when flakes of titanium dioxide are deposited sometimes. Such precipitates are often colored pale yellow by a little peroxide in the ether. If the titanium content is low, a clear solution is obtained which is usually brownish yellow on account of the formation of a little pertitanic acid by peroxide in the ether. The precipitation of titanium dioxide during the ether treatment is due to hydrolysis and is caused by the fact that ether removes some of the hydrochloric acid which was necessary to prevent hydrolysis;[1]

$$\overset{\leftrightarrow}{Ti}^{++} + 4H_2O \rightleftarrows Ti(OH)_4 + 4H^+$$

Under the proper conditions, the quantity of iron remaining with the titanium after the ether separation in the aqueous solution is very small. Evaporate off the dissolved ether by heating on the water bath and continue the evaporation to dryness. Add a little concentrated hydrochloric acid to the residue, whereby some of the titanium remains undissolved as TiO_2, dilute to 150 cc. without filtering and add 3 g. of solid ammonium acetate. Heat the solution to boiling and keep gently boiling for a few minutes. All the titanium is then precipitated as dioxide contaminated with ferric basic acetate. Allow the precipitate to settle and then filter. Test the filtrate with hydrogen peroxide to see if any titanium remains. If so, boil the solution 15 min. longer. Wash the precipitate with water containing ammonium acetate, ignite and weigh. The precipitate is almost always contaminated with some iron. The true titanium content may be determined by one of the three following methods.

(a) **Colorimetric Determination.**—Fuse the ignited titanium oxide precipitate with 15–20 times as much of previously dehydrated potassium pyrosulfate, $K_2S_2O_7$, which is prepared by heating potassium acid sulfate in a platinum crucible until fumes of sulfuric anhydride are evolved. After fusing, cool the crucible and dissolve the melt in 75 cc. of cold water and 5 cc. of concentrated sulfuric acid. If an insoluble residue remains it must be fused again with potassium pyrosulfate. Dilute the solution

[1] If the concentration of the hydrochloric acid was six-normal (*i.e.* sp. gr. 1.1), there is little danger of any TiO_2 being precipitated. Care must be taken not to dilute the solution much below this concentration.

to 100 cc. in a calibrated flask and use 50 cc. or less, according to the titanium content, for the colorimetric comparison.

To prepare a standard solution of titanium, weigh 0.4996 g. of pure anhydrous potassium titanium fluoride, K_2TiF_6, into a platinum crucible. To remove fluorine and form potassium sulfate and titanium sulfate, heat the salt with a little water and concentrated sulfuric acid until fumes are evolved, and repeat the treatment several times. Finally dissolve the titanium sulfate by heating with a little concentrated sulfuric acid and dilute with 5 per cent. sulfuric acid to 100 cc. One cubic centimeter of this solution contains 0.001 g. of titanium. Or, the standard solution may be prepared by fusing 0.1665 g. of pure titanium dioxide with 8 times as much sodium carbonate, dissolving up the excess sodium carbonate in cold water, filtering and dissolving the residue of sodium acid titanate in 10 cc. of concentrated sulfuric acid and finally diluting the solution to exactly 100 cc. at room temperature. One cubic centimeter of standard solution contains 0.001 g. titanium.[1]

Prepare a series of standards by measuring out 1, 3, 5, 10-cc., etc., portions of the standard titanium solution, diluting each to 50 cc. in a Nessler tube with 5 per cent. sulfuric acid, adding 2 cc. of hydrogen peroxide (free from fluorine) and mixing. Compare with the standards the color produced with an aliquot part of the solution to be analyzed and 2 cc. of hydrogen peroxide. The color in the case of dilute solutions may be compared by looking down upon the tubes against a white background. Another method is to place the tube side by side in a colorimeter with a weaker standard and dilute the unknown solution with measured volumes of 5 per cent. sulfuric acid, mixing after each addition, until the two solutions are of the same color and dilution. In this case the tubes are held side by side and viewed horizontally. From the known amount of titanium present in the standard it is easy to compute that present in the unknown solution.

This colorimetric method is the most satisfactory for the

[1] The standard solution can be prepared even more easily by digesting 0.1665 g. of pure titanium oxide with 10 cc. of hot concentrated sulfuric acid in a porcelain dish. When the oxide has all dissolved, cool and very carefully dilute to exactly 100 cc. at room temperature. Usually the acid gently ignited to titanium oxide obtained in the analysis can be dissolved by digesting with hot concentrated sulfuric acid.

determination of small quantities of titanium. In most cases a satisfactory analysis can be made with a sample of iron or steel weighing only 1 g. The method is not suitable for large amounts of titanium, as the color of the pertitanic acid is best estimated in dilute solutions and when more than 1 per cent. of titanium is present a very small aliquot part of the sample has to be taken. The solution should contain at least 5 per cent. of sulfuric acid when the test is made and molybdenum, vanadium or chromium must not be present as each of these elements gives a color reaction with hydrogen peroxide. The test is so delicate that one part of titanium can be detected in the presence of one million parts of water.

Computation.—If n_2 cc. of the standard solution match the color produced with n_1 cc. of the 100-cc. solution obtained from s g. of metal, then

$$\frac{10n_2}{s \times n_1} = \text{per cent. Ti}$$

Or, if it was necessary to dilute n_1 cc. of the analyzed solution with t cc. of 5 per cent. sulfuric acid before getting a shade corresponding to n_2 cc. of standard in 50 cc. of solution, then

$$\frac{0.2(n_1 + t)n_2}{n_1 \times s} = \text{per cent. Ti}$$

(b) Volumetric Determination.—Fuse the impure titanium oxide in a platinum crucible with about 10 times its weight of sodium carbonate. Cool, place the crucible in a beaker and cover it with cold water. After all the sodium carbonate has dissolved, filter off the solution from the insoluble sodium acid titanate and ferric oxide and wash the residue with cold water. Allow the funnel to drain completely, pierce the filter with a pointed glass rod, and wash the precipitate into a small Erlenmeyer flask with dilute hydrochloric acid (sp. gr. 1.12). Wash the filter with hot hydrochloric acid of the same strength and heat this acid with the residue until all the sodium titanate and ferric oxide have dissolved. Acid more dilute than this will not dissolve the precipitate. If this point is forgotten and water is added, hydrolysis takes place and the titanium is precipitated. Such a precipitate is very hard to filter and wash so that it is very easy to spoil the analysis at this point.

Concentrate the solution to about 20 cc. in a 200 cc. Erlenmeyer flask. Add 10–20 cc. of concentrated hydrochloric acid (sp. gr. 1.2) and close the flask with a rubber stopper carrying a Bunsen valve on the outside. To make a Bunsen valve, insert a piece of glass tubing into a one-hole rubber stopper and on the glass tubing place a short piece of rubber tubing sealed at the other end with a piece of stirring rod. Make a slit in the side of the tubing to permit gas to escape from the flask; pressure from the outside squeezes the cut ends of the rubber together so that air from the outside cannot enter the flask. Better still, the flask may be connected, as shown in Fig. 130, with a beaker containing a saturated solution of sodium bicarbonate.[1] Then if there is any back pressure, sodium bicarbonate is sucked into the flask which causes evolution of carbon dioxide and thus prevents air from entering.

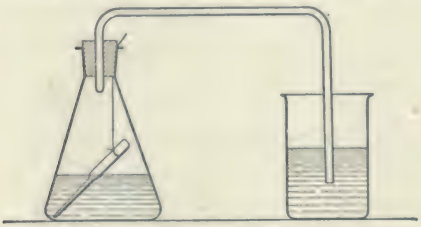


FIG. 130.

To reduce the titanium from the quadrivalent to trivalent condition, introduce a piece of 50 per cent. zinc-magnesium alloy, weighing about 2 g. or about 3 g. of stick zinc in coarse pieces. It is not necessary that the zinc should be absolutely free from iron. Stopper the flask and allow the reduction to take place for a time in the cold. When the solution has become violet and most of the zinc has dissolved, add 1 or 2 g. more of the metal, in coarse pieces, close the flask quickly, and finish the reduction by heating on the water bath.

During the reduction, the following reaction takes place:

$$2Ti^{++}_{++} + Zn(\text{or } Mg) = 2Ti^{+++} + Zn^{++}(\text{or } Mg^{++})$$

To accomplish the reduction, it is necessary to get all of the quadrivalent titanium into the ionic condition. In attempting to reduce a slightly acid titanium solution, the reduction is usually incomplete on account of hydrolysis even when there is no visible precipitation of titanium dioxide, for the hydrated oxide

[1] A Contat-Göckels valve works very nicely. See Z. angew. Chem., **13,** 620 (1899), or Treadwell-Hall, Analytical Chemistry II, 601 (3d edition).

may remain in colloidal solution. In such cases the titration will give too low results. For this reason, it is necessary to have the titanium solution strongly acid to get a complete reduction.

Instead of using a small quantity of zinc and waiting till all has dissolved, a larger piece of metal may be used and suspended in the solution, as shown in the drawing, by means of fine platinum wire. After reducing for three-quarters of an hour to an hour, allow the solution to cool and then remove the excess of zinc, rinsing it with cold water.

Add to the solution 1 or 2 g. of pure ammonium thiocyanate, free from iron, and titrate with ferric chloride solution until a permanent red color, due to ferric thiocyanate, is obtained.

Computation.—If n cc. of ferric chloride solution, of which 1 cc. $= t$ g. of titanium, are used in the analysis of a sample weighing s g., then

$$\text{per cent. Ti} = 100t\frac{n}{s}$$

or, in case the ferric chloride solution was exactly tenth-normal,

$$\text{per cent. Ti} = \frac{n}{s}\,0.481$$

(c) Determination of Iron in Impure Titanium Oxide.—Inasmuch as the impurity present in the ignited precipitate of titanium oxide is chiefly ferric oxide, the quantity of titanium dioxide may be estimated with fair accuracy by determining the amount of iron by titration and then deducting the corresponding amount of ferric oxide from the weight of impure titanium oxide.

The volumetric determination of the iron may be accomplished in the hydrochloric acid solution obtained after fusing the impure titanium oxide with sodium carbonate (p. 310) by the iodometric method described on p. 307, or by the following method, in which tenth-normal permanganate is used.

Titanium is reduced from the quadrivalent to trivalent condition less readily than iron is reduced from the ferric to ferrous state. Thus metallic zinc, which is so often used for reducing ferric solutions previous to titration with permanganate, begins to reduce titanium after the ferric ions are all reduced and the reduction is more or less complete according to the conditions. If the conditions are as described in the previous method, a quantita-

tive reduction of both iron and titanium takes place. Stannous chloride, recommended on p. 307, also reduces titanium solutions, although it is possible, with a little practice, to reduce the iron and practically no titanium, by stopping the addition of the reagent at the exact point where the solution becomes colorless; further addition of stannous chloride causes the formation of violet, trivalent titanium ions.

Probably the most satisfactory reducing agent, however, for reacting with ferric ions in the presence of titanium is hydrogen sulfide in sulfuric acid solution.

Procedure.—Fuse the impure titanium dioxide with potassium pyrosulfate and dissolve the melt as directed on p. 309. Transfer the solution to a 200-cc. flask which is fitted with a rubber stopper carrying two glass tubes by which gas can enter and leave the flask. The tubes are each bent once at right angles and the one through which the hydrogen sulfide is to enter reaches nearly to the bottom of the flask, while the other extends just to the lower edge of the rubber stopper. The solution to be reduced should contain about one-tenth its volume of concentrated sulfuric acid. Heat the solution to boiling while passing hydrogen sulfide gas through it. With the small amount of iron present, a few minutes should suffice for the complete reduction of the ferric ions. Continue boiling the solution gently and replace the stream of hydrogen sulfide with one of carbon dioxide and pass this gas through the solution until it ceases to blacken lead acetate paper as it leaves the flask. Cool in a slow stream of carbon dioxide and titrate with potassium permanganate.

Computation.—If p g. of impure TiO_2 were obtained in the analysis of s g. of the original material and the only impurity was ferric oxide which required n cc. of permanganate which was f-normal, then

$$\text{per cent. Ti} = 60.05\,\frac{(p - 0.7985\,n.f)}{s}$$

2. DETERMINATION OF TITANIUM IN INSOLUBLE MATERIALS

(Ferro-titanium and other Titanium Alloys)

Procedure.—Fuse 1–2 g. of the material, which should be pulverized as finely as possible, in a platinum crucible with 5 or

6 times as much of a mixture of 1 part magnesium oxide and 2 parts of anhydrous sodium carbonate (*cf.* p. 178). Mix the sample with the fusion mixture and introduce it into the crucible after first covering the bottom with a layer of the fusion mixture. Carry out the fusion as directed on p. 179.

Transfer the ignited mass to an agate mortar, moisten it with a little cold water and triturate to a paste. Rinse the paste into a beaker using as little water as possible. Add to the contents of the beaker 5 or 6 times as much concentrated hydrochloric acid (sp. gr. 1.2) as there is water in the beaker, cover with a watch-glass to prevent loss by spattering, and heat gently, stirring from time to time. If the directions are carefully followed, a clear solution will be obtained in a short time.

Concentrate the hydrochloric acid solution, transfer it to a 200 cc. Erlenmeyer flask, reduce with zinc and titrate as described on p. 312.

If the titanium content is high it may be advisable to use an aliquot part of the solution. In this case do not concentrate the hydrochloric acid solution of the melt, but dilute it with hydrochloric acid (sp. gr. 1.12) to 250 cc. in a calibrated flask and use 100 cc. for the titration, first concentrating the solution.

In some cases muddy, violet-colored solutions are obtained after the reduction with zinc. This is due to some impurity such as molybdenum or tungsten. In such cases it is advisable to proceed somewhat differently in order to remove the impurities. Extract the product of the first fusion with hot water and wash the insoluble residue of magnesium oxide and sodium acid titanate very thoroughly with hot water. Ignite the filter and its contents in a platinum crucible till the filter is all consumed, mix the residue with 3 or 4 times as much sodium carbonate as the original sample weighed, and again heat strongly. Remove the melt from the crucible with the aid of a little cold water, and dissolve in hydrochloric acid as described above.

Test Analyses. 1. *Experiments with Titanium Solutions.*—A titanium solution was prepared and titanium dioxide determined by precipitation from acetic acid solution. Duplicate experiments gave 0.0961 and 0.0978 g. TiO_2 corresponding respectively to 0.0577 and 0.0587 g. Ti.

Twenty cubic centimeters of titanium solution were mixed

with 30 cc. of ferric chloride solution (= 4.8 g. Fe) and the iron removed by the ether separation. The titanium was precipitated from acetic acid solution and the iron titrated by the iodometric method. In one experiment 0.1007 g. of impure TiO_2 were obtained and the iron present required 0.4 cc. of tenth-normal sodium thiosulfate solution, corresponding to 0.0032 g. Fe_2O_3. The corrected weight of TiO_2 was thus 0.0975 g. corresponding to 0.0586 g. Ti.

In a similar experiment the corresponding values were—0.0993 g. impure TiO_2, 0.2 cc. sodium thiosulfate = 0.0016 g. Fe_2O_3, 0.0977 g. pure TiO_2 and 0.0587 g. Ti.

Twenty cubic centimeters of the titanium solution were titrated with ferric chloride; 1 cc. of $FeCl_3$ = 0.004912 g. Ti. In duplicate experiments 12.18 and 12.10 cc. of the ferric chloride solution were used, corresponding to 0.0598 and 0.0594 g. Ti.

Thirty cubic centimeters of titanium solution were mixed with 30 cc. of ferric chloride solution, the iron was removed by ether, the titanium precipitated as dioxide, and the titanium determined by titration in the hydrochloric acid solution obtained after fusing the impure titanium dioxide with sodium carbonate. In one experiment 12.10 cc. and in another 12.05 cc. of ferric chloride solution were required, corresponding to 0.0594 and 0.0592 g. Ti.

Titanium Determinations by Method 2

Duplicate determinations with 2-g. samples of metallic titanium using one-fifth of the solution for the final titration, required respectively 50.5 and 50.7 cc. of ferric chloride (1 cc. = 0.004995 g. Ti) corresponding to 63.0 and 63.3 per cent. Ti.

With ferro-titanium (Goldschmidt) the values 18.9 and 19.0 per cent. Ti were obtained with samples weighing 1 g.

In a sample of cast iron, the titanium was determined gravimetrically, simply purifying the titanium dioxide by heating with sulfuric and hydrofluoric acids to remove silica. The values obtained with 10-g. samples were 0.070 and 0.067 per cent. Ti.

Accuracy of the Results and Permissible Deviations

Small quantities of titanium may be separated from iron by the ether process and the titanium precipitated as dioxide. The

volumetric determination of small quantities of titanium is not at all reliable but the results by the colorimetric method are excellent. Results should agree within the following limits:

Per cent. Ti	Permissible Deviation
0.05– 0.2	±0.02 per cent.
0.2 – 1.0	±0.03 per cent.
1.0 – 5.0	±0.1 per cent.
5.0 –10.0	±0.2 per cent.

CHAPTER XIII

IRON

In the analysis of a sample of ordinary steel the percentage of iron is usually determined most accurately by deducting the percentages of other constituents from 100. In the analysis of special steels and ferro alloys, however, it is often important to have an accurate and rapid method for determining the iron directly. A great many methods are known for the accurate determination of iron but unfortunately nearly all of them are influenced by some of the other elements which are found in steel alloys. For this reason it is hard to give general directions which will be applicable in all cases and sometimes the errors involved in separating iron from a number of possible interfering elements are such as to influence seriously the final determination.

Thus the small amount of carbon present in the iron wire that is so frequently used for standardization may influence the volumetric determination to the extent of several tenths of 1 per cent., unless special precautions are taken, such as gently boiling the solution or oxidizing with strong permanganate before attempting to reduce the solution previous to the titration with permanganate. Similarly, the errors in the gravimetric determination of iron are often considerable. Thus vanadium, titanium, aluminium and molybdenum may be precipitated with ferric oxide and the ammonia used may contain dissolved silica which will be precipitated when poured into the acid solution and thus contaminate the ferric hydroxide precipitate. Moreover, there is difficulty in igniting the ferric oxide; if it is heated too hot, especially when all the carbon is not consumed, some magnetic oxide is formed, and if the precipitate is not washed free from chloride some ferric chloride may be volatilized.

1. DETERMINATION OF IRON IN MATERIALS SOLUBLE IN ACID

(a) Mohr's Iodometric Method

The method, which depends upon the reduction of the iron with potassium iodide in slightly acid solution, has already been de-

scribed on p. 307, for the standardization of a ferric chloride solution.

The determination of the iron can usually be combined with the determination of some other constituent. Thus the ether solution obtained in the determination of manganese, chromium, nickel and cobalt, aluminium, titanium, vanadium, etc., may be used for the iron determination. If an ethereal solution of ferric chloride is exposed to the light, particularly direct sunlight, for any length of time, some of the ferric chloride becomes reduced to ferrous chloride. In such cases the solution should be oxidized and the excess of oxidizing agent removed before attempting to determine the iron by the iodometric process.

Shake the ethereal solution in the Rothe shaking funnel with several portions of water, transferring the washings to a tall beaker, then wash a few times with dilute hydrochloric acid, until finally the addition of a fresh portion of hydrochloric acid shows no further yellow color of dissolved ferric chloride and the upper ether layer is perfectly colorless. Evaporate off the dissolved ether by heating on the water bath and concentrate to a small volume.

Dilute the solution to 500 cc. in a calibrated flask, mix thoroughly, and take an aliquot portion corresponding to about 0.25 g. of iron.

Pour the slightly acid solution into a 300 cc. Erlenmeyer flask, add 3 g. of pure potassium iodide, free from iodate, and titrate the liberated iodine with tenth-normal thiosulfate solution. Add the thiosulfate slowly from the burette until only a slight color remains in the iron solution, then add 2 cc. of starch solution (*cf.* p. 207) and titrate until the blue color disappears. When completely decolorized, the blue color may return after a little while on account of the fact that the last traces of ferric chloride are reduced very slowly by hydriodic acid at the room temperature. To hasten this decomposition, heat the solution to 50°, or 60° at the most; in a short time all of the iron will be reduced to the ferrous condition. Cool the flask under the water tap and finish the titration with sodium thiosulfate, adding a little more starch.

To the amount of iron thus obtained, a correction must be added corresponding to the iron remaining in the aqueous layer after treatment with ether and also for that remaining with the

silica and obtained as ferric oxide after the volatilization of the silicon fluoride. Fuse this residue with a little sodium carbonate and dissolve the melt in a little dilute hydrochloric acid, setting aside the solution. In the aqueous solution obtained after the ether separation, precipitate the iron as basic ferric acetate, by neutralizing the solution with ammonia, making acid with acetic acid and boiling the dilute solution with 3 g. of ammonium acetate. Dissolve the precipitate in hydrochloric acid and add the solution to the iron solution obtained from the silica residue. Evaporate off the excess of acid and carry out the iodometric determination of the iron.

Instead of taking the ethereal solution of ferric chloride, the solution remaining in the flask after the evolution method for determining sulfur (p. 259) may be used, or the solution obtained after the determination of copper (p. 263). After the removal of the copper, which is always necessary when appreciable amounts of copper are present because cupric salts react with potassium iodide (*cf.* p. 267), concentrate the solution by evaporation and carefully oxidize the iron by adding nitric acid, drop by drop, or potassium chlorate (about 4 g. for 10 g. of iron). Evaporate the solution with concentrated hydrochloric acid to remove the excess of oxidizing agent and carry out the iodometric determination in an aliquot part of the diluted solution.

Computation.—Assuming that n cc. of f-normal sodium thiosulfate were used in titrating the iron in a sample representing s g. of the original material, then

$$\text{Per cent. Fe} = \frac{n \times f \times 5.585}{s}$$

(b) Zimmermann-Reinhardt Method

Procedure.—In an aliquot portion of the original solution, obtained as described in the above method, determine the iron by titration with permanganate solution after reducing with stannous chloride, removing the excess of stannous chloride with mercuric chloride and adding manganous sulfate and phosphoric acid solution exactly as described on p. 307 for the standardization of a ferric chloride solution.

2. DETERMINATION OF IRON IN INSOLUBLE MATERIALS

Procedure.—Fuse the finely pulverized material with magnesia-sodium carbonate mixture in a platinum crucible as described on p. 178. Extract the melt with hot water, whereby chromate, vanadate and other substances that may interfere are dissolved in the form of sodium salts of the corresponding acids, and the iron remains behind as insoluble ferric oxide. Wash the residue thoroughly and determine the iron by either of the above volumetric methods.

If the original material contained no appreciable amount of disturbing substances such as chromium, vanadium or molybdenum, the fusion may be dissolved at once in dilute hydrochloric acid and the solution used for the titration.

If copper is present to an appreciable extent, the acid solution should be saturated with hydrogen sulfide, the copper sulfide precipitate filtered off and the iron determined in the filtrate as described on p. 320.

With materials rich in titanium, the fused product obtained after ignition with magnesia-sodium carbonate mixture should be dissolved directly with concentrated hydrochloric acid (sp. gr. 1.2) or, if it is desired to remove the soluble sodium salts, the melt should be extracted with *cold* and not hot water as otherwise it is difficult to get a clear solution with hydrochloric acid. Any pertitanic acid that may form during the solution of the melt will be reduced during the subsequent evaporation.[1] In this case the iodometric method should be used, or the iron should be reduced with hydrogen sulfide (*cf.* p. 314).

Test Analyses. (*a*) *Determination of Iron in* 23 *Per Cent. Nickel Steel.*—Using samples weighing 0.5 g. and carrying out the ether separation and titration with sodium thiosulfate, the results obtained in duplicate experiments were 75.6 and 75.6 per cent. Fe.

(*b*) *Iron in Ferro-vanadium with* 25.7 *Per Cent. V.*—Using 4.0-g. samples and one-twentieth of the solution for the final titration, the values obtained were 71.5 and 71.6 per cent. Fe.

(*c*) *Iron in* 50 *Per Cent. Ferro-vanadium, Rich in Carbon.*—The results obtained in duplicate experiments using the ether

[1] Knecht and Hibbert, J. Soc. Chem. Ind., **30**, 396.

separation and sodium thiosulfate titration were 31.2 and 31.0 per cent. Fe.

In another experiment the sample was fused with magnesia-sodium carbonate mixture and the sodium thiosulfate titration showed 31.3 per cent. Fe.

(*b*) *Iron Phosphide with* 24.9 *Per Cent. P.*—Using 1.0 and 0.51-g. samples and taking three-tenths of the solution for the titration after the fusion with magnesia-sodium carbonate, the results obtained were 74.5 and 74.7 per cent. Fe.

(*e*) *Titanium Metal,* 63 *Per Cent. Pure.*—Experiments with the fusion method, followed by sodium thiosulfate titration, gave the values 2.99 and 3.05 per cent. Fe.

Accuracy of the Method and Permissible Deviation in the Values

If the iodometric method for the determination of the iron is carefully carried out, the following agreement of the results can be obtained.

Iron Content	Permissible Deviation
0.1 to 0.5 per cent	0.02
0.5 to 2.0 per cent	0.03
2.0 to 10.0 per cent	0.05
10.0 to 25.0 per cent	0.10
25.0 to 50.0 per cent	0.15
50.0 to 100.0 per cent	0.20

CHAPTER XIV

TUNGSTEN

Tungsten is not found very often in steels. It is never present as impurity but is intentionally added in special alloy steels such as high-speed steels in quantities up to 20 per cent. or even more.

1. DETERMINATION OF TUNGSTEN IN MATERIALS SOLUBLE IN ACID

(a) Precipitation as Tungstic Acid Anhydride, WO_3, in Hydrochloric Acid Solution

Principle.—On treating a steel containing tungsten with an oxidizing acid solvent, all the tungsten is converted into tungstic acid anhydride, WO_3. The precipitation of this substance may be made quantitative from hydrochloric acid solutions provided precautions are taken to prevent some of it remaining in the colloidal condition as hydrosole.

Procedure.—If the material is low in tungsten use a 10-g. sample, otherwise use 5 g. or less. Weigh the sample into a porcelain casserole and dissolve it in dilute nitric acid (sp. gr. 1.2) using 110 cc. for a 10-g. portion and 60 cc. for a 5-g. portion. The material should be in the form of fine turnings. Steels with much tungsten often resist the action of nitric acid, but in most cases they may be dissolved slowly by adding a few drops of concentrated hydrochloric acid, waiting till all action has ceased, and repeating the addition of hydrochloric acid from time to time.

Evaporate the solution to dryness and heat the residue to decompose the nitrates. When no more nitrous fumes are evolved by strongly heating the residue, cool it somewhat, moisten with concentrated hydrochloric acid (sp. gr. 1.2) and heat gently with 50 cc. of hydrochloric acid (sp. gr. 1.12) until finally all the ferric oxide has dissolved. The residue of silica and tungstic acid

anhydride should not be colored red with ferric oxide after this treatment with hydrochloric acid. Again evaporate the solution to dryness on the water bath and heat the residue at 135° till no more acid vapors are evolved. Then moisten the residue once more with concentrated hydrochloric acid and dissolve all the iron by heating with six-normal hydrochloric acid, but do not continue heating after all the basic ferric chloride has dissolved. Evaporate off the excess of hydrochloric acid, continuing the process as far as possible without causing solid to separate out; in this way a thick sirup is obtained. It is necessary to follow these directions carefully in order to make the precipitation of the tungsten quantitative.

Allow the thick sirup to cool and then dilute with an equal volume of dilute hydrochloric acid (1 part conc. acid to 5 parts water), stir and allow to stand a few minutes. Filter off the deposited silica and tungsten trioxide through an ashless filter. Rinse the precipitate from the dish to the filter by means of dilute hydrochloric acid from a wash bottle. Usually, when tungsten is present, a yellow film of tungsten trioxide remains adhering to the porcelain dish. After washing the dish and filter with dilute hydrochloric acid till free from iron, rub the dish with a filter paper moistened with ammonia water and add the paper to the contents of the filter; the ammonia dissolves the yellow tungsten trioxide forming ammonium tungstate which is converted back to the oxide upon ignition. Finally rub the dish with a piece of filter paper moistened with alcohol.

If the tungsten content is high the residue often filters badly. It is a good plan in such cases to add, before filtering, a little filter paper pulp prepared by shaking small pieces of filter paper with hot water; this prevents the pores of the filter from becoming immediately clogged with fine precipitate. Traces of tungsten trioxide may pass through the filter and sometimes the turbidity thus produced is scarcely noticeable. In all cases, therefore, evaporate the filtrate in a 250 cc. beaker as far as possible without causing solid salts to deposit and allow the liquid to cool. Then, if any tungsten trioxide has passed through the filter, it will settle out on the bottom of the beaker and be distinctly visible. To recover such a precipitate, dilute as before and filter through a fresh filter.

The filtrate may now be used for the determination of other elements such as manganese, nickel, chromium, phosphorus, etc.

Heat the filters and precipitates at a low temperature till all the carbon is consumed and finally ignite to a constant weight over the full heat of the Bunsen or Tirrill burner. The crucible must not be heated over the blast lamp because at high temperatures tungstic acid is volatilized slowly.

After weighing the precipitate of silica and tungsten trioxide, moisten it with about 5 drops of sulfuric acid (1 : 1) and add about 2 cc. of hydrofluoric acid. Evaporate as far as possible on the water bath, or preferably in an air bath, and then heat very carefully with the free flame until the sulfuric acid is expelled. Finally heat strongly with the same burner that was used for heating the impure tungsten trioxide. The loss in weight corresponds to the amount of silica, SiO_2, present and from this the quantity of silicon in the steel can be computed. The residue in the crucible, however, cannot be regarded as pure tungsten trioxide. It is invariably contaminated with a little ferric oxide and may contain some mangano-manganic oxide, Mn_3O_4, chromic oxide, Cr_2O_3, titanium dioxide, TiO_2, and possibly traces of vanadium pentoxide, V_2O_5, or molybdenum trioxide, MoO_3.

To purify the precipitate, fuse it with about 6 times as much sodium carbonate. Extract the fused mass with a little water, wash the crucible and its cover carefully, and filter off the insoluble residue upon a small filter. Wash the precipitate thoroughly with hot water and then ignite it in the same crucible, without attempting to clean it after washing out the soluble sodium salts. The residue contains all the iron and titanium that contaminated the tungsten trioxide; in most cases the weight of this residue subtracted from the previous weight of impure tungsten trioxide obtained after the removal of the silica, will give the weight of pure tungsten trioxide. For the direct determination of the tungsten, the sodium tungstate solution, which may be contaminated with chromium as shown by a yellow colored solution, is treated with mercurous nitrate solution in the following manner.

Add a piece of litmus paper to the solution in a 300–400-cc. beaker, cover the beaker with a watch glass to prevent loss by effervescence, and carefully neutralize the solution with dilute

nitric acid (1 part concentrated acid to 5 parts of water). Expel all the carbonic acid from the solution by boiling gently and then add to the hot, neutralized solution some mercurous nitrate reagent (p. 290) until no further precipitation is produced. Stir the solution and continue the boiling for a short time. Allow the precipitate to settle and test with a little more mercurous nitrate to see if the precipitation was complete. Again heat to boiling, allow the precipitate to settle and add 2 or 3 drops (not more) of six-normal ammonia (sp. gr. 0.96). This addition of ammonia serves to neutralize the acid of the mercurous nitrate solution (*cf.* p. 290). If the ammonia is not added some of the tungsten may remain dissolved as metatungstate. On the other hand, if too much ammonia is added, this will cause some of the precipitate to dissolve. Many chemists, therefore, prefer not to use ammonia and add instead a paste containing precipitated mercuric oxide stirred up with water. Then, by heating the solution with this paste, the excess of acid can be neutralized.

The addition of the few drops of ammonia should cause the formation of a black precipitate, $Hg\begin{matrix}NH_2\\NO_3\end{matrix}$ + Hg, showing that an excess of mercurous ions is present in the solution. Stir the solution well and boil for a short time. The precipitate should retain its gray color during the boiling; if it becomes yellow again it is necessary to add a little more ammonia and treat as before.

Allow the precipitate to settle and then decant the clear solution through an ashless filter. When all the clear solution has been poured through the filter, cover the precipitate with hot water and add a few cc. of mercurous nitrate solution. Boil a short time and again decant the solution through the filter. Continue this treatment once or twice more in order to remove all the soluble alkali salts. Then transfer the precipitate to the filter and wash a few times with hot water.

The precipitate adhering to the sides of the beaker can usually be removed by rubbing it with a moist piece of filter paper; in case it has dried to the sides of the beaker and is hard to remove, use a filter moistened with a little nitric acid. Place the filter

paper used for wiping out the beaker in a weighed platinum crucible and burn this paper by itself, allowing the air to enter the crucible freely. Then add the main precipitate while still moist on the filter and ignite carefully under a good hood. This ignition may take place without danger in a platinum crucible provided plenty of air is allowed to enter the crucible.

After the filter paper is all consumed, ignite the contents of the crucible to constant weight over a Bunsen or Terrill burner.

If the solution is colorless before the addition of the mercurous nitrate solution, there is no chromium present and the contents of the crucible usually consists of practically pure tungsten trioxide of light yellow color. A green coloration may be caused by the presence of a little alkali or of a trace of molybdenum trioxide.

If the solution was yellow before the addition of the mercurous nitrate solution, chromium is present and the ignited tungsten trioxide contains chromium and has a greenish-gray color.

As the tungsten was originally precipitated from strongly acid solution, it seldom happens that much chromium is present at this stage of the analysis. After weighing the impure tungsten trioxide, the chromium may be determined by fusing the residue with sodium carbonate, dissolving the melt in water, acidifying with hydrochloric acid and treating with potassium iodide and sodium thiosulfate solution (p. 292) or the residue in the crucible may be fused with the potassium acid tartrate mixture (p. 294) and the sodium tungstate, now free from chromium, washed out with water. The weight of chromic oxide, Cr_2O_3, obtained by computation from the volume of sodium thiosulfate used, or by direct weighing of the residue after the potassium acid tartrate fusion, deducted from the weight of impure tungsten trioxide, gives the weight of the pure substance. The uncolored filtrate from the potassium acid tartrate fusion may be used for the direct precipitation of the tungsten or, in special cases, for the determination of vanadium and molybdenum.

Computation.—If p represents the weight of pure tungsten trioxide obtained in the analysis of s g. of material then

$$\text{per cent. W} = \frac{p}{s} 79.31$$

(b) Separation of Tungsten from Iron by Sodium Peroxide Fusion[1]

Principle.—If a mixture of ferric oxide and tungstic acid anhydride is fused with sodium peroxide, the latter is converted into soluble sodium tungstate and may be separated from the ferric oxide by extracting the melt with water. The tungsten may be precipitated by means of mercurous nitrate but the mercurous tungstate will be contaminated by mercurous phosphate, chromate, vanadate and molybdate to the extent that phosphorus, chromium, vanadium and molybdenum are present in the original material; a little silica is also likely to be carried down. The precipitate, therefore, must undergo further treatment in order to obtain pure tungsten trioxide.

Procedure.—Weigh out 2 g. of tungsten steel containing about 5 per cent. tungsten, or 1 g. of a steel richer in tungsten, into a small porcelain casserole. Cover the casserole with a watch-glass and treat the steel with 30 cc. of nitric acid (sp. gr. 1.2). When the steel is dissolved, evaporate the solution to dryness and heat the residue, keeping the dish covered with a watch-glass, until no more nitrous fumes are evolved. The oxides then become detached, for the most part, from the sides of the dish.

Transfer the oxides as completely as possible to an agate mortar and mix them with 6 or 8 times as much pure sodium peroxide. Add the mixture to a nickel crucible. Sprinkle a little more sodium peroxide in the original dish and add this to the contents of the crucible. Dissolve any tungsten in the residue, that remains adhering to the dish, by heating with a little caustic soda solution and add this solution to that which is eventually obtained from the sodium peroxide fusion.

Heat the mixture in the nickel crucible with a very small flame until the flux is melted and continue the heating for about half an hour, heating just hot enough to keep the sodium peroxide liquid. After allowing the crucible to cool, place it in a beaker and add just enough water to cover the crucible. Heat the water to hasten the solution of the melt and when all is dissolved, remove the crucible and wash it out with hot water. Dilute the solution

[1] Hinrichsen, Mitt. Kgl. Materialprüfungsamt, **25**, 308 (1907) or Stahl u. Eisen, **27**, 1418 (1907).

to about 200 cc. and, if it appears green in color after the ferric hydroxide has settled out, add a little sodium peroxide from the blade of a knife; this serves to reduce sodium manganate to manganese dioxide. Allow the precipitate to settle completely and decant the clear solution through a filter, catching the filtrate in a 250 cc. calibrated flask. Wash the precipitate in the beaker by pouring dilute sodium carbonate solution (2 g. per 100 cc. water) upon it, allow the precipitate to settle, and decant the liquid through the filter. Repeat the washing several times until certain that all the sodium tungstate has been dissolved. Then cool the filtrate to room temperature and dilute to the mark. Mix the solution thoroughly and take an aliquot part for the further analysis, *e.g.*, two-fifths. Transfer the aliquot part of the solution to a beaker of about 350 cc. capacity and precipitate with mercurous nitrate solution, exactly as described on p. 326. Treat the precipitate with sulfuric and hydrofluoric acids to remove the silica and continue the purification process as described on p. 327.

Instead of determining the chromium in the same sample, it is a little easier to take another aliquot part of the solution and determine the chromium in it according to p. 292. By multiplying the weight of chromium thus obtained by the factor 1.462, the corresponding weight of chromic oxide is obtained; deduct this from the weight of the impure tungsten trioxide.

If vanadium and molybdenum are present, these elements must be determined by methods to be described in the sections of this book which immediately follow. Corresponding quantities of V_2O_5 and MoO_3 must be deducted from the weight of impure tungsten trioxide.

If much phosphorus is present it must also be determined and allowance made. As a rule, however, the phosphorus content of tungsten steel is not over 0.03 per cent. and the error resulting from neglecting it is not serious.

2. DETERMINATION OF TUNGSTEN IN MATERIALS INSOLUBLE IN ACID

(*Ferro-tungsten, Metallic Tungsten*)

Principle.—Iron alloys rich in tungsten may be analyzed by treatment with magnesia-sodium carbonate mixture (p. 178)

provided the metal is brittle enough to be powdered. The tungsten is thereby converted to sodium tungstate which dissolves in water.

Procedure.—Mix from 1 to 3 g. of the finely powdered material in an agate mortar with 6 or 8 times as much of Eschka mixture and heat in a platinum crucible for about an hour over a Méker burner. After cooling, extract the sintered mass in a beaker with hot water. If the solution is colored green by sodium manganate, add a little sodium peroxide and heat the solution to precipitate the manganese as dioxide. Filter off the sodium tungstate after allowing the precipitate to settle. Wash the residue on the filter with hot water, then transfer it to the same platinum crucible that was used before, smoke off the filter and fuse again with about 4 times as much Eschka mixture as the original weight of the material. By a second fusion of an hour, all the tungsten is converted to sodium tungstate unless the material was too coarse.

The well-washed residue may be used for the determination of iron and manganese.

Dilute the combined filtrates in a 500 cc. calibrated flask and determine the tungsten in an aliquot part of the solution by the method described on p. 325. If the filtrate obtained after fusion is yellow, chromium is present; in such cases determine the chromium in another aliquot part of the solution (p. 292 *et seq.*) and deduct the corresponding weight of chromic oxide, Cr_2O_3, from the weight of impure tungsten trioxide. If vanadium and molybdenum are present, these elements must also be determined (pp. 333 and 343).

The method just described can be used for the determination of tungsten in metallic tungsten. In most cases, however, it is more important to know how much *metallic* tungsten an alloy contains rather than to know the total tungsten content, whether as metal or oxide, or combined with other non-metallic elements. By deducting the impurities from 100, the percentage of metallic tungsten can be found.

To determine the iron, manganese, lime, calcium and magnesia, fuse from 2 to 4 g. of the finely powdered metal with 6 times as much pure sodium carbonate, placing the mixture in a platinum crucible which already contains a little sodium carbonate on

the bottom. Heat the fusion mixture an hour or two over a Bunsen burner keeping the contents of the crucible just below the fusion temperature. Finally raise the temperature and heat over the blast lamp for a short time. In this way a satisfactory fusion can be made. After dissolving the melt in water, and heating with a little sodium peroxide, the residue contains ferric oxide, manganese dioxide, nickel oxide, calcium carbonate and magnesium carbonate to the extent that these elements were present in the metallic tungsten. Some of the iron usually adheres to the sides of the crucible; dissolve this by warming with hydrochloric acid. All these substances in the residue are determined in the usual way. Further impurities are carbon, silicon, oxygen combined with iron or tungsten (for which a corresponding weight of ferric oxide or tungsten trioxide is deducted), phosphorus, chromium, vanadium molybdenum, aluminium, water-soluble alkali tungstate, etc. These elements are determined as described in the corresponding chapters of this book.

Test Analyses.—A solution of sodium tungstate was prepared and the tungsten determined by precipitation with mercurous nitrate. In duplicate determinations the values 0.0681 and 0.0682 g. WO_3 were obtained in 25 cc. of solution.

Twenty-five-cubic-centimeter portions of this sodium tungstate solution were mixed with two portions of ferric chloride solution, corresponding to 1.6 and 3.2 g. of metallic iron, and the determination of the tungsten carried out by Method 1*a*. The values obtained in the analysis were 0.0683 and 0.0682 gm. WO_3. An equally close agreement was obtained when only 5 cc. of the sodium tungstate solution were used.

In two other experiments, tungstate solution corresponding to 0.0204 g. WO_3 was mixed with ferric chloride solution corresponding to 5 g. of Fe and sodium silicate solution corresponding to 0.0541 and 0.1082 g. SiO_2. In these experiments 0.0739 and 0.1268 g. of $WO_3 + SiO_2$ were obtained and, after the volatilization of the silica, 0.0200 and 0.0193 g. WO_3.

A sample of tungsten steel was analyzed by Method 1*a* and by Method 1*b*. In the former case only about 0.001 g. of Cr_2O_3 contaminated the WO_3 precipitate but in the latter case 0.0342 g. of Cr_2O_3 was present. After making the correction for chromium,

the values obtained were 5.83 and 5.88 by Method 1*a* and 5.71 and 5.75 by Method 1*b*.

Another sample, which was difficultly soluble in nitric acid, was dissolved by adding several portions of concentrated hydrochloric acid to the nitric acid solution; the contamination of the tungsten precipitate was in one case just as large in Method 1*a* as in Method 1*b*. The values obtained in the analysis of this steel were 4.29 and 4.20 per cent. W by Method 1*a* and 4.17 and 4.34 by Method 1*b*.

A steel richer in tungsten was analyzed by Method 1*b* and there was but little contamination by chromium. The corrected values obtained were 18.84 and 18.83 per cent. W.

Accuracy of the Method and Permissible Variations

Small quantities of tungsten can be detected qualitatively, but it is not easy to estimate quantities less than 0.02 per cent. W. As a rule, the following agreement can be obtained in duplicate determinations:

Tungsten Content	Permissible Deviation
0.2 – 0.5 per cent.	± 0.02 per cent.
0.5 – 1.0 per cent.	± 0.03 per cent.
1.0 – 5.0 per cent.	± 0.05 per cent.
5.0 – 10.0 per cent.	± 0.08 per cent.
10.0 – 20.0 per cent.	± 0.10 per cent.

CHAPTER XV

VANADIUM

Small quantities of vanadium are often present in cast iron owing to the presence of vanadium in the iron ore. Vanadium is oxidized very easily and for that reason is used, like aluminium and titanium, as a deoxidizing agent in the manufacture of steel. When the amount of vanadium added is small, the greater part of it passes into the slag so that the finished steel is often greatly benefited and yet does not contain any vanadium. Special steels, on the other hand, often contain vanadium as an essential part of the alloy.

1. DETERMINATION IN IRON AND STEEL BY THE ETHER METHOD

(a) Iodometric Determination

Principle.—Vanadium, like manganese and many other metals, can be separated from ferric chloride in hydrochloric acid solution by shaking the solution with ether. If, however, the separation is carried out exactly as described for manganese, it sometimes happens that a little vanadium follows the iron into the ether; this vanadium may be removed from the ether solution by shaking with hydrochloric acid (sp. gr. 1.1) that has been saturated with ether, and adding a few drops of hydrogen peroxide, which forms pervanadic acid, insoluble in ether.

The vanadium may be separated from manganese, nickel, etc., by an oxidizing fusion (*cf.* p. 189) and from chromium by heating with potassium acid tartrate mixture (p. 294). In the aqueous extract the vanadium may be determined iodometrically by the method of Holverscheit.[1] The vanadic acid, containing quinquevalent vanadium, is reduced by the action of hydrobromic acid to either hypovanadic acid or vanadyl salt, probably the

[1] Dissertation, Berlin, 1890.

latter, in which the vanadium is quadrivalent. The reaction may be expressed as follows:

$$2V^{+++} + 2Br^{-} = 2V^{++} + Br_2$$

or,

$$2HVO_3 + 2KBr + 6HCl = 2VOCl_2 + 2KCl + Br_2 + 4H_2O$$

The bromine is distilled into potassium iodide solution and the liberated iodine is titrated with standard thiosulfate solution. The equation shows that 1 atom of vanadium loses one valence charge and is equivalent to 1 atom of bromine; it follows, therefore, that 1 cc. of normal sodium thiosulfate solution is equivalent to 0.0510 g. of vanadium.

Inasmuch as the vanadium content of iron and steel is usually very low, it is advisable to use an approximately fiftieth-normal solution, prepared by taking 100 cc. of tenth-normal sodium thiosulfate, standardized as described on p. 206, 268 or 287, and diluting to exactly 500 cc. in a calibrated flask. The titer of the well-mixed solution is then one-fifth of the original solution.

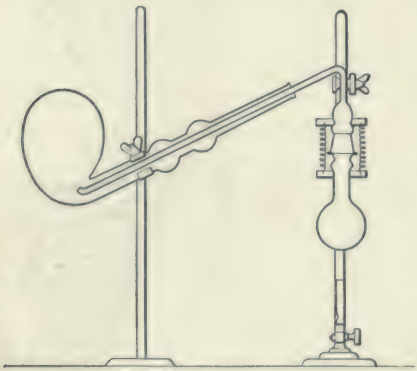


FIG. 131.

Necessary Apparatus and Solutions.—The Rothe shaking apparatus and ether-hydrochloric acid solutions are described on p. 184. For distilling off the iodine and catching the vapors in potassium iodide solution, the Bunsen apparatus shown in Fig. 131 is used.

Procedure.—Weigh out 10–15 g. of the material into a porcelain evaporating dish and dissolve in dilute nitric acid (sp. gr. 1.2). Remove the silica by Method B (p. 173) or the determination may be hastened as described on p. 200. In the filtrate from the silica, remove the ferric chloride by shaking with ether as described on p. 185. To remove traces of vanadium from the ethereal solution of ferric chloride, shake the latter 3 or 4 times

with the 10-cc. portions of ether-hydrochloric acid (sp. gr. 1.10) and 3–5 drops of 3 per cent. hydrogen peroxide solution, instead of with ether-hydrochloric acid alone.

Ether usually contains a little peroxide, and this suffices, when the vanadium content is low, to give a reddish-brown coloration to the aqueous solution first obtained on shaking with ether. If more vanadium is present the vanadium solution first obtained is bluish green or blue. If much vanadium is present the ether solution will usually contain an appreciable quantity of vanadium; when this is the case, dark brown flocks will be noticed on adding the hydrogen peroxide to the olive-green ferric chloride solution in ether.

After the removal of the iron, treat the solution exactly as described on p. 189, finally fusing with sodium hydroxide and sodium peroxide, and dissolving the fused mass in water.

Filter off the oxides of manganese and nickel and boil the filtrate, which is yellow if chromium is present, to decompose the excess of peroxide. Neutralize the solution with dilute nitric acid and precipitate the vanadium with mercurous nitrate solution exactly as described under Chromium (p. 293). Test the colorless filtrate with more mercurous nitrate solution to see if the precipitation was complete. If no more precipitate is formed, acidify the filtrate with nitric acid and add a few drops of hydrogen peroxide; if all the vanadium was precipitated there will be no brown coloration of pervanadic acid. The precipitate contains all the vanadium and chromium together with some phosphorus. After filtering and washing the precipitate, ignite it together with the filter in a platinum crucible, fuse with potassium acid tartrate mixture (*cf.* Chromium, p. 294), and extract the product of the fusion with a little hot water.

If considerable residue was obtained after heating the mercurous salt, it is advisable to fuse this last residue of chromic oxide with potassium acid tartrate again. The fusion may be accomplished in the same way as before, or the chromic oxide may be fused with pure sodium carbonate and then enough potassium acid tartrate added to reduce all the chromium to chromic oxide. Extract the fused product with hot water and add the solution to that previously obtained. Wash the residual chromic oxide

and carbon with hot water until the soluble alkali salts are all dissolved.

Concentrate the aqueous solution of the sodium vanadate to about 35 cc. and transfer it to the decomposition flask of the Bunsen apparatus (Fig. 131), washing out the beaker several times with a little water and keeping the total volume of liquid as small as possible.

Neutralize the solution in the flask by the cautious addition of concentrated hydrochloric acid (free from chlorine) and add about 30 cc. of the concentrated acid in excess to the solution which is now yellow in color. Introduce about 3 g. of pure potassium bromide and at once connect the apparatus as shown in the drawing, placing a concentrated solution of pure potassium iodide (from 5 to 10 g. free from iodate) in the receiver. Arrange the apparatus so that the receiver can be turned in the clamp to let air escape during the distillation. The tube which leads from the distilling flask to the iodine solution should have an opening from 1 to 2 mm. in diameter.

Gradually heat the liquid in the flask to boiling and allow the air to escape, from time to time, by turning the receiver. After the distillation begins, shown by the fact that the vapors are absorbed with a hissing noise, continue heating for about 10 min. longer. The yellow solution in the distilling flask changes to green and finally blue when all the quinquevalent vanadium has been reduced to the quadrivalent condition. Then, before taking the flame away, detach the receiver from the clamp and remove it from the delivery tubing; after this the flame may be withdrawn without danger of the solution sucking back. Cool the contents of the receiver under running water, rinse it into an Erlenmeyer flask, and titrate the free iodine with sodium thiosulfate solution, adding starch solution toward the last. To make certain that there is no unchanged vanadate in the decomposition flask, fill the receiver with fresh potassium iodide solution and repeat the distillation.

Computation.—If n cc. of f-normal sodium thiosulfate solution were used in titrating the vanadium in a sample weighing s g., then

$$\text{per cent. V} = \frac{n \times f \times 5.10}{s}$$

(b) TITRATION OF VANADIUM WITH POTASSIUM PERMANGANATE[1]

Principle.—The vanadium is separated from the iron as in the previous method and from chromium by precipitation with sodium hydroxide. The vanadium is then precipitated in acetic acid solution by means of lead acetate. The lead vanadate is dissolved in hot hydrochloric acid, the vanadium reduced to vanadyl salt by boiling with hydrochloric acid and the vanadyl salt is oxidized with potassium permanganate. The reactions may be expressed as follows:

$$Pb_3(VO_4)_2 + 6HCl = 3PbCl_2 + 2H_3VO_4$$
$$2H_3VO_4 + 6HCl = 2VOCl_2 + 6H_2O + Cl_2$$
$$VOCl_2 + H_2SO_4 = VOSO_4 + 2HCl$$
$$5VOSO_4 + KMnO_4 + 11H_2O = 5H_3VO_4 + KHSO_4 + MnSO_4 + 3H_2SO_4$$

Procedure.—Carry out the ether separation exactly as described in the previous method and remove the dissolved ether by evaporating on the water bath. Add nitric acid in excess and evaporate to remove the hydrochloric acid. When the solution is almost sirupy, add 20 cc. of hot water and heat with a few drops of sulfurous acid solution to reduce any chromic acid that may have been formed. Boil and slowly pour the hot solution, stirring vigorously, into a boiling solution of sodium hydroxide (100 g. NaOH to the liter; 1 cc. of this solution will neutralize about 2.4 cc. of nitric acid, sp. gr. 1.2). Boil the solution a few minutes, allow the precipitate to settle, filter, and wash the precipitate until it is free from alkali. The precipitate contains the hydroxides of chromium, nickel and iron, copper and manganese while the vanadium remains in the filtrate as sodium vanadate. To remove traces of chromium that may be left in the filtrate, slightly acidify with dilute nitric acid, make alkaline with sodium hydroxide and boil again. If any more precipitate is formed, filter, and make the filtrate acid with acetic acid. Heat the filtrate to boiling, add an excess of lead acetate solution (usually 10 cc. is sufficient) and boil for several minutes. Filter off the precipitate of yellow lead vanadate and wash it with hot water. Dissolve the precipitate by pouring hot dilute hydrochloric

[1] *cf.* A. A. Blair, J. Am. Chem. Soc., **30**, 1228.

acid through the filter.[1] Evaporate nearly to dryness, add 50 cc. of hydrochloric acid (sp. gr. 1.2), and again evaporate nearly to dryness. Finally add 10 cc. of concentrated sulfuric acid and evaporate until the acid fumes freely. Cool, dilute to 150 cc., heat to between 60° and 70°, and titrate slowly with dilute permanganate solution.

Computation.—If n cc. of f-normal permanganate were used in titrating the vanadium in a sample weighing s g., then as on p. 336,

$$\text{per cent. V} = \frac{n \times f \times 5.10}{s}$$

NOTES.—Campagne[2] has shown that good results can be obtained by this reduction with hydrochloric acid when not more than 0.1 g. of vanadium is present. Gooch and Stockey[3] have also shown that the reduction by means of hydrochloric acid is practically complete. Rosenheim[4] and Holverscheidt,[5] however, have claimed that the results are a little low, and that the reduction by means of sulfurous acid is safer. With this reagent the reduction is accomplished by boiling the solution, which contains sulfuric acid, while passing sulfur dioxide through it until the solution appears a pure blue, showing that the vanadic acid has been reduced to vanadyl salt. Continue the boiling and replace the stream of sulfur dioxide with one of carbon dioxide, until the vapors when led into a dilute solution of potassium permanganate will no longer decolorize it. Then titrate the hot solution with permanganate.

This method may be carried out after a previous titration with permanganate, so that it may be used as a check upon the other method.

Müller and Diefenthaler,[6] in the analysis of ferro-vanadium found that the reduction by means of hydrochloric acid alone did not always give dependable results. They found that much depended upon the exact manner in which the evaporation was conducted and that different values were obtained after evaporation in an Erlenmeyer flask than when an open porcelain evaporating dish was used. They regard the reduction with sulfurous acid as the standard method but find that nearly as good results can be obtained by evaporating with hydrochloric acid

[1] If there is much precipitate, remove the lead by evaporating to dryness, moistening the residue with hydrochloric acid, and treating with alcohol. Filter off the lead chloride and evaporate off the alcohol; the vanadium will then be present entirely as vanadyl salt.

[2] Ber., **36,** 3164.

[3] Chem. News, **87,** 133; Z. anorg. Chem., **32,** 456.

[4] Ann., **251,** 197.

[5] Inaug. Diss., Berlin, 1890.

[6] Z. anorg. Chem., **71,** 243 (1911).

and alcohol. The procedure they recommended for the analysis of ferro-vanadium is as follows:

Weigh about 1 g. of the finely divided alloy into a covered beaker and dissolve it in a little concentrated nitric acid. Evaporate to remove the excess nitric acid, add a little concentrated hydrochloric acid and evaporate nearly to dryness to change the ferric nitrate into ferric chloride. Add 20 cc. more of concentrated hydrochloric acid and 50 cc. of alcohol and evaporate, by gently boiling the solution, to about 5 cc. Rinse the solution into a calibrated flask and determine iron in one aliquot part and the vanadium in another.

Determine the iron by the iodometric method given on p. 318. The results are usually about 0.5 per cent. too high.

Determine the vanadium by titrating the cold solution with permanganate, using the manganese sulfate reagent as in the determination of iron by the Zimmerman-Reinhardt method (p. 308).

2. DETERMINATION OF VANADIUM AFTER A FUSION

Principle.—The finely powdered material is fused with a suitable alkaline flux, the alkali vanadate thus formed is dissolved in water, and then determined as in the above methods. To make sure that the residue insoluble in water contains no vanadium, it is advisable to fuse it a second time.

If it is impossible to reduce the original material to a powder, it is best to treat first with nitric acid, evaporate the nitrates to dryness, convert them into oxides by ignition, and then carry out the fusion.

Procedure.—Mix 1–2 g. of the finely powdered material in an agate mortar with 6 times its weight of Rothe magnesia-sodium carbonate mixture (1 : 2) and heat the mixture in a platinum crucible as described on p. 178.

With samples which are not brittle enough to powder, dissolve 2–3 g. in a small porcelain dish with nitric acid (sp. gr. 1.2), evaporate the solution, heat to decompose the nitrates, and fuse the residue in a nickel crucible with 12–18 g. of sodium peroxide (*cf.* p. 298).

In both cases, extract the product of the fusion with water; if the solution is colored green by manganate, reduce the latter to manganese dioxide by adding a little sodium peroxide.

Then filter off the insoluble residue through an ashless filter, wash it thoroughly with hot water, and ignite the filter with its

contents in a platinum crucible. Mix the residue with 3–6 g. of sodium carbonate, again fuse and extract with hot water, adding the solution to that previously obtained.

The combined filtrates contain all the vanadium as sodium vanadate in the presence of sodium phosphate, chromate, tungstate, etc. Neutralize the solution with nitric acid and treat with mercurous nitrate solution as described on p. 293.[1]

If the vanadium content is high, so that a large mercurous precipitate is to be expected, dilute the solution in a calibrated flask and use an aliquot part for the treatment with mercurous nitrate.

Filter off the precipitate, ignite, and fuse the oxides with sodium carbonate and acid potassium tartrate as described on p. 294. Extract the fusion with water, filter off the chromic oxide and carbon, and concentrate the filtrate to a small volume. Neutralize the solution with hydrochloric acid and distil with potassium bromide as described on p. 334.

Or, instead of determining the vanadium iodometrically, the aqueous solution which has been freed from chromium may be evaporated with hydrochloric acid and the reduced vanadyl salt determined by titrating with permanganate (*cf.* p. 337).

3. GRAVIMETRIC DETERMINATION OF VANADIUM[2]

Principle.—Ammonium metavanadate, NH_4VO_3, is insoluble in a cold, saturated solution of ammonium chloride. By ignition, it is changed into vanadium pentoxide, V_2O_5.

The ammonium chloride method of precipitating vanadium cannot be used in the presence of tungstate.[3] If chromate is present, some chromate is precipitated with the vanadium and some vanadium is not precipitated, so that in many cases the correct value is obtained by compensation. The presence of phosphate, arsenate, molybdate or sulfate does not seriously interfere.

Procedure.—If tungsten is present start the analysis according

[1] If no chromium is present, the aqueous solution is colorless. In such a case, the vanadium can be determined directly without previous precipitation with mercurous nitrate. Acidify the solution at once with hydrochloric acid and transfer to the evolution flask.

[2] *cf.* Gooch and Gilbert, Z. anorg. Chem., **32,** 175 (1902); E. Campagne, Ber., **1903,** 3164.

[3] Rosenheim, Z. anorg. Chem., **32,** 181 (1902).

to Method 1*a*, dissolving about 5 g. of the material, removing the silica and tungsten from hydrochloric acid solution, the iron by shaking with ether, and fusing in a platinum dish, etc. In the absence of iron, Method 2 may be used.

In the absence of tungsten, Method 2 may be used for starting the analysis.

Ignite the mercurous nitrate precipitate, obtained by either of these methods, and remove the chromium by the sodium carbonate and potassium acid tartrate fusion. Neutralize the aqueous extract of the fusion with nitric acid and decolorize the yellow solution by adding a little ammonia and heating. Estimate the approximate volume of the solution and, if it seems advisable, concentrate it somewhat.

To the cold solution add, all at once, 2.5 g. of pure ammonium chloride for each 10 cc. of solution and stir vigorously to dissolve the salt. The solution becomes colder, a turbidity forms, and gradually white flocks of ammonium metavanadate are precipitated. When this procedure is followed there is little tendency for the precipitate to attach itself to the sides of the beaker.

Allow the solution to stand at least 8 hr., then filter and wash the precipitate with cold, 25 per cent. ammonium chloride solution. Ignite the precipitate in a platinum crucible, finally melting the vanadium pentoxide.

After weighing the oxide, V_2O_5, boil it with a little concentrated sodium hydroxide solution. It should dissolve in the alkali without leaving any residue. The purity of the precipitate may be tested by pouring the solution into the Bunsen apparatus, acidifying and distilling with potassium bromide, as described on p. 334.

Computation.—If p g. of vanadium pentoxide were obtained from a sample weighing s g., then

$$\text{per cent. V} = 56.04\,\frac{p}{s}$$

Test Analyses. (*a*) *Experiments with Sodium Vanadate Solution.*—Fifty cubic centimeters of the solution were treated with mercurous nitrate solution and on ignition 0.3051 g. of V_2O_5 were obtained.

Ten cubic centimeters of the solution required 6.65 cc. of sodium thiosulfate solution; according to this, 50 cc. = 0.3030 g.

When using 25- and 50-cc. portions of the solution, the results obtained by iodometric titration corresponded in each case to 0.3034 g. V_2O_5 in 50 cc.

Twenty-five cubic centimeters of solution precipitated with ammonium chloride gave 0.1528 g. V_2O_5; 50 cc. of solution would contain, therefore, 0.3056 g. V_2O_5.

The ammonium chloride process was carried out with 25-cc. portions of sodium vanadate solution in the presence of 1-g. portions of each of the following salts: potassium acetate, sodium nitrate, sodium sulfate, sodium phosphate, potassium arsenate, ammonium molybdate, potassium chromate and sodium tungstate. With each of the first five salts the values ranged from 0.1520 to 0.1528 g. of V_2O_5, which agreed satisfactorily with the theoretical value, 0.1526 g. V_2O_5. With ammonium molybdate, the precipitation of the vanadium was complete but the precipitate contained about 2 mg. of impurity. With the chromate about the same excess weight was obtained and the filtrate contained a little vanadium. In the presence of tungsten, the precipitate weighed about 3 mg. too little and contained tungsten.

(*b*) *Separation of Vanadium and Iron by the Ether Process.*—Ten cubic centimeters of a vanadium solution, prepared by dissolving vanadium pentoxide in hydrochloric acid, contained 0.2300 g. V_2O_5.

When mixed with ferric chloride solution, corresponding to 3.2 g. of metallic iron, the ammonium chloride precipitate yielded 0.2304 g. V_2O_5. With ferric chloride corresponding to 6.5 g. of iron, the value was 0.2295 g. V_2O_5.

(*c*) *Determination of Vanadium in Different Materials.*—The analysis of a cast iron by the ammonium chloride process, using 4-g. samples gave 0.029 per cent. and 0.025 per cent. V.

Another specimen of cast iron was analyzed by Method 1*a* and the values obtained with 5-g. samples were 0.139 per cent. and 0.133 per cent. V.

An alloy steel containing tungsten, chromium, molybdenum and vanadium was analyzed by Method 1*a* and the values obtained with 5-g. samples were 2.14 and 2.17 per cent. V.

CHAPTER XVI

MOLYBDENUM

Molybdenum is seldom present as impurity in iron or steel but is sometimes added intentionally. Ferro-molybdenum, chrome-molybdenum and metallic molybdenum are used in the preparation of special steels.

Principle.—Iron and molybdenum cannot be separated from one another by the ether method. Blair[1] has shown that practically all the molybdenum follows the ferric chloride into the ether. The best way of separating molybdenum and iron is probably by a suitable fusion method whereby the molybdenum is converted into soluble alkali molybdate and the iron is left behind as insoluble ferric oxide. In the aqueous solution the molybdenum may be precipitated as sulfide and the molybdenum determined as oxide after igniting the sulfide. Molybdenum sulfide, MoS_3, belongs to the group of sulfides which are insoluble in acid but soluble in alkaline sulfide solutions.

Procedure.—If the material can be pulverized, fuse 1–2 g. of the powder with 6 times as much of Rothe magnesia-sodium carbonate mixture (1 : 2), at not too high a temperature, and extract the ignited product with hot water (p. 179). Of steel filings or drillings, dissolve 2–3 g. in nitric acid (sp. gr. 1.2), destroy the nitrates as described on p. 298, and fuse the oxides with sodium peroxide in a nickel crucible at a relatively low temperature.

After extracting with water, filter off the undissolved oxides, wash well and fuse again with 3–6 g. pure sodium carbonate in a platinum crucible. Extract the product of this fusion with water and add the filtered solution to that previously obtained.

The filtrates now contain beside all the molybdenum, any vanadium, tungsten, phosphorus, silicon, etc., that was originally present. If the molybdenum content is considerable, dilute up

[1] J. Am. Chem. Soc., **30**, 1228.

to the mark in a calibrated flask and use an aliquot part of the well-mixed solution for the further analysis. If the molybdenum content is small, use the entire solution.

Neutralize the greater part of the alkali with dilute sulfuric acid, evaporate the solution to 50–100 cc., add 25 cc. of strong ammonia, and saturate the solution with ammonium sulfide. Then acidify with dilute sulfuric acid and warm the solution while passing hydrogen sulfide gas through it. In this way there is no difficulty in precipitating all the molybdenum as sulfide.

If tungsten is present, add tartaric acid to the solution before making it acid. This prevents the precipitation of tungsten.[1]

Filter off the precipitate of molybdenum sulfide and wash the precipitate with very dilute sulfuric acid and finally with water. Ignite the precipitate with the filter in a weighed porcelain crucible at as low a temperature as possible.[2]

Heat the crucible at first with a very low flame so that the point of the flame just touches the crucible, placing this flame at the front of the crucible until all the moisture is expelled and then at the base of the crucible, so that escaping hydrocarbons will not take fire. Turn the crucible a little from time to time to hasten the decomposition into molybdenum oxide, MoO_3. Finally, when all but a little of the carbon has been consumed, dissolve the oxide in a little ammonia, add a few crystals of ammonium nitrate, evaporate carefully to dryness, and ignite until all the ammonium salts are volatilized. If necessary, repeat this treatment till all the carbon is consumed.

If vanadium is present, the molybdenum trioxide has a dark color. After weighing the oxides, dissolve them in a little caustic soda solution and determine the vanadium by Method 1*a* or 1*b*. Deduct the corresponding amount of vanadium pentoxide (1 cc. normal solution = 0.0091 g. V_2O_5) from the weight of impure molybdenum oxide.

If arsenic is present, it may be removed by precipitating the ammoniacal solution with magnesia mixture before precipitating the molybdenum; the arsenic is precipitated as magnesium ammonium arsenate, which on ignition is changed to magnesium pyroarsenate, $Mg_2As_2O_7$.

[1] Friedheim and Meyer, Z. anorg. Chem., **1**, 76 (1892).

[2] *Cf.* Friedheim and Euler, Ber., **28**, 2061 (1895).

The filtrate from the hydrogen sulfide precipitation will have a violet or bluish-green color if chromium and vanadium are present. It may be tested again with hydrogen sulfide to see if the precipitation of the molybdenum sulfide was complete.

Pure molybdenum oxide has a light yellow color when cold. On adding a drop of sulfuric acid and evaporating off the excess acid, a beautiful blue color is obtained.

Computation.—If p g. of pure molybdenum trioxide were obtained from s g. of steel, then

$$\text{per cent. Mo} = \frac{66.67 \times p}{s}$$

NOTE.—The molybdenum may be determined in the ether solution obtained as on p. 185.[1] The procedure is as follows:

Evaporate the ether solution nearly to dryness, add 10 cc. of concentrated sulfuric acid and again evaporate to remove the hydrochloric acid. Cool, dissolve in about 100 cc. of water and reduce the ferric salt by adding ammonium bisulfite. Boil off the excess of sulfurous acid and cool the solution. Transfer it to a 200-cc. pressure bottle, saturate with hydrogen sulfide gas, stopper the bottle, and heat on the water bath for several hours. Allow the solution to cool slowly, open the bottle, and filter off the molybdenum sulfide. Ignite it as described above and weigh the pure molybdenum oxide, MoO_3.

[1] A. A. Blair, J. Am. Chem. Soc., **30**, 1228.

CHAPTER XVII

OXYGEN

Ingot iron, or mild steel, often contains combined oxygen. The amount of oxides present depends upon the extent to which decarburization has been effected by oxidation in the manufacture of the material.

The oxygen is present chiefly as ferrous oxide dissolved in the crystals of ferrite but it may be present as other oxide enclosed in the metal. In 1882 Ledebur[1] proposed a method for the determination of oxygen based upon the reduction of the oxide at a red heat by hydrogen and weighing the water thus formed. Ledebur's method is the one that has been used most for the determination of oxygen in iron and steel but although it reduces quantitatively the oxides of iron, molybdenum, tungsten, etc., to the metallic state, any oxygen combined with manganese, aluminium, silicon, titanium, etc., escapes the determination, or at least for the most part. In 1912, W. H. Walker and W. A. Patrick[2] published a method by which nearly all oxides are reduced. The metal is heated in an electric vacuum furnace with graphite and the carbon monoxide formed is determined.

1. LEDEBUR'S METHOD

To obtain accurate results, it is necessary that the original material be perfectly dry and free from organic matter and that the hydrogen be free from oxygen.

Apparatus.—The hydrogen may be prepared from a Finkener generator,[3] a Kipp generator or by the electrolysis of dilute sul-

[1] Stahl u. Eisen, **2,** 193 (1882); Leitfaden für Eisenhütten-Laboratorien, p. 105 (1900).

[2] J. Ind. Eng. Chem., **4,** 799 (1912); 8th Intern. Congr. Appl. Chem., **21,** 139 (1912).

[3] Fig. 132, at the extreme right.

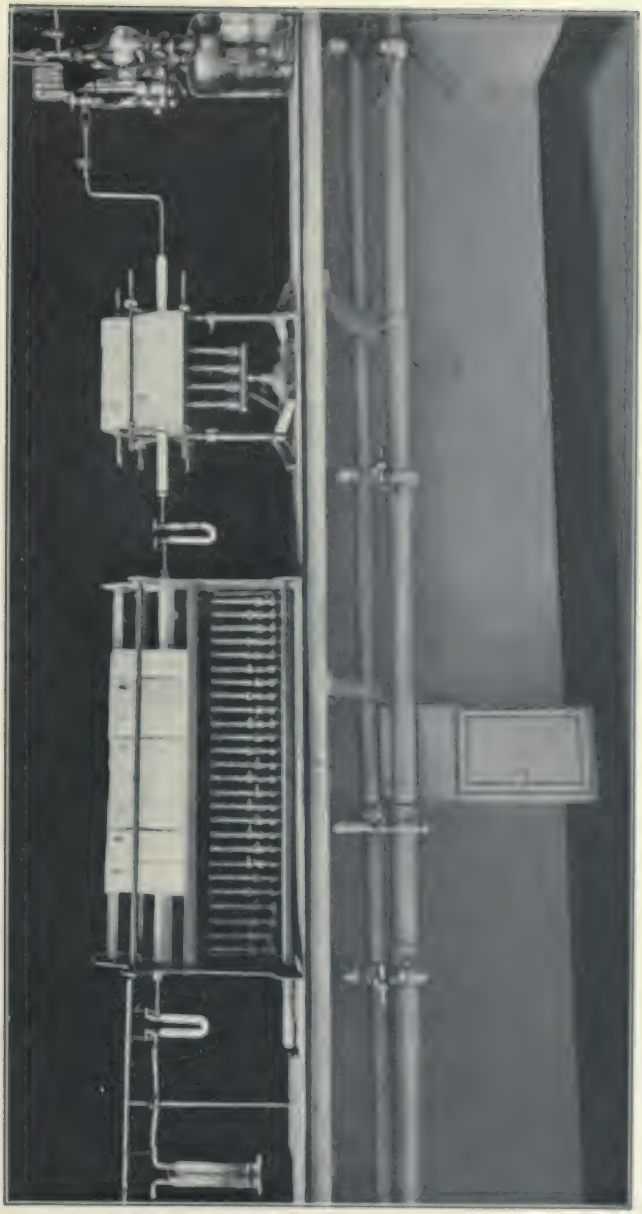


FIG. 132.—Apparatus for the determination of oxygen.

furic acid. The gas is washed to remove impurities[1] and then, to remove any possibility of traces of oxygen remaining, it is passed through a hot porcelain tube containing platinized asbestos. The water obtained from the union of hydrogen and oxygen in this tube is removed by passing the gas through a U-tube containing phosphorus pentoxide between plugs of glass wool.

The thoroughly purified and dried gas then enters the porcelain combustion tube in which the sample is to be heated and the water formed from the oxygen in the sample is absorbed in a weighed tube containing phosphorus pentoxide. To prevent contamination of the latter from moisture in the atmosphere, this last absorption tube is connected with a bubble tube containing a little concentrated sulfuric acid; this tube also serves to indicate the rate at which the gas is passing through the apparatus.

Procedure.—Special pains must be taken with the sample to be used in this determination. To remove organic substances such as oil or grease, wash the borings with chloroform, alcohol and ether using reagents which are free from non-volatile residue. Select borings free from rust or scale, unless it is desired to determine the oxygen in such portions of the metal. Finally, dry the sample by heating in a hot closet at 105° and cool in a desiccator.

Before starting the analysis proper, it is necessary to carry out a blank experiment with the apparatus all in place and using the same procedure as in the analysis itself; this is to make sure that there is no gain in weight in the phosphorus pentoxide tube owing to impurities in the hydrogen, to leaky apparatus, or to moisture in the tube.

Pass a current of hydrogen through the entire apparatus without, at first, heating either of the porcelain tubes. After 30 or 45 min. collect a little of the escaping gas in a test tube and test it to see if it will burn quietly. If this is the case, light the burners under the tube containing the platinized asbestos and keep this

[1] In Fig. 132, the purification train consists of a tube containing 50 per cent. caustic potash solution (to remove HCl, H_2S, etc.), a tube containing alkaline pyrogallol solution (about 3 per cent. pyrogallol in 10 per cent. caustic potash: this serves to remove oxygen) and a tube containing concentrated phosphoric acid (to remove most of the moisture).

Instead of pure caustic potash solution, Ledebur recommends a solution of lead oxide in caustic potash.

tube hot as long as a continuous stream of hydrogen is being passed through the apparatus. Detach the phosphorus pentoxide tube, allow it to stand near the balance for 15 min. and weigh. Again connect this tube with the apparatus and heat the empty combustion tube to redness during a period of 30 to 45 min. Then turn out the burners under this tube and allow it to cool while the current of hydrogen is still passing. Detach the absorption tube, allow it to stand at least 15 min. near the balance and again weigh it. If this second weight is within 1 mg. of the first weight, the apparatus is ready for the combustion of the sample.

Weigh out 15 g., or more, of the metal into a porcelain boat. If it is desired to use a larger quantity of the material, weigh it upon a watch-glass, dry in a closet at 105° for an hour, cool in a desiccator, and weigh again. If heating for half an hour longer causes no further loss in weight, introduce the sample into the combustion tube which has already been heated in a current of hydrogen. Large samples may be introduced directly into the combustion tube between plugs of ignited asbestos. Before heating or connecting the absorption tube, pass the hydrogen through the apparatus for an hour in order to remove all traces of atmospheric oxygen. Then connect the weighed absorption tube and begin to heat the tube containing the sample. Gradually raise the temperature till a bright red heat is obtained and keep the tube at this temperature for about 30 min., then turn down the flames and allow the furnace to cool. Finally detach the absorption tube, allow it to stand near the balance for at least 15 min. and weigh.

After the furnace has cooled down with the hydrogen still passing through it, the oxidized sample can be removed from the tube and the apparatus is ready for a new determination.

Computation.—If s represents the weight of sample taken for analysis and p the weight of water obtained in the absorption tube, then

$$\frac{p \times \mathrm{O} \times 100}{\mathrm{H_2O} \times s} = 88.81 \frac{p}{s} = \text{per cent. oxygen}$$

Applicability of the Method.—Besides serving for the determination of oxygen in iron, the method can be used with a fair degree

of accuracy for determining the extent to which a sample of material has rusted and for determining the amount of combined oxygen in samples of metallic tungsten or molybdenum, or in the alloys of these elements with iron.

Test Analyses. 1. *Determination of Oxygen in Mild Steel.*—Using 40-g. samples the values 0.018 and 0.020 per cent. O were obtained in duplicate determinations with one sample and the values 0.016 and 0.015 per cent. with another.

Determination of Rust on Cast-iron Borings.—The borings were composed of coarse particles and of very fine particles. By means of sieves the borings were sorted into three portions according to fineness. Fifteen grams of borings gave 6.795 g. of finest chips, 4.747 g. of coarser chips and 3.456 g. of coarsest chips. Using these proportions of the material the values 2.60 and 2.50 per cent. O were obtained by combustion of a 15 g. composite sample.

3. *Determination of the Oxygen Content of Ferrotungsten.*—Ten-gram portions of the dried and powdered material gave duplicate results of 0.056 and 0.050 per cent. O.

4. *Determination of the Oxygen Content of Powdered Tungsten.*—Duplicate determinations with samples weighing about 30 g. gave the values 0.044 and 0.043 per cent. O.

5. *Oxygen in Metallic Tungsten and in Metallic Molybdenum.*—The combustion in hydrogen of two different samples of tungsten showed 0.46 and 0.52 per cent. O and with two different samples of molybdenum the values 0.22 and 0.59 per cent. O were obtained; 10-g. samples were used in each case.

2. METHOD OF WM. H. WALKER AND W. A. PATRICK[1]

Apparatus.—A vacuum furnace of the Arsem type (Fig. 133), having a capacity of about 325 cc. capacity, is recommended.[2] The gun-metal chamber *A* rests inside a water jacket *R*. The cover *B* is fastened to the chamber by means of 18 cap screws, *D*, and the joint is made tight by a rigid lead gasket. The tube, *J*, through which the furnace is exhausted, is soldered into the cover. The window *G* is fastened by the cover to six cap-screws and the joint is made tight by another lead washer. The mica window *E*

[1] J. Ind. Eng. Chem., **4**, 799 (1912); 8th Intern. Congr. Appl. Chem., **21**, 139.

[2] General Electric Co., Schenectady, N. Y., *cf.* J. Am. Chem. Soc., **28**, 921 (1906).

is placed in the top of the window tube. The brass tubes *W*, through which water flows, serve as electrodes. Between the electrodes the graphite heater *L* is fastened by means of clamps *U*. The crucible containing the substance is supported on the stand shown in the drawing and is thus placed in the hottest part of the furnace.

For evacuating the furnace a small rotary oil pump in series with a Geryk pump[1] works satisfactorily and will give a vacuum

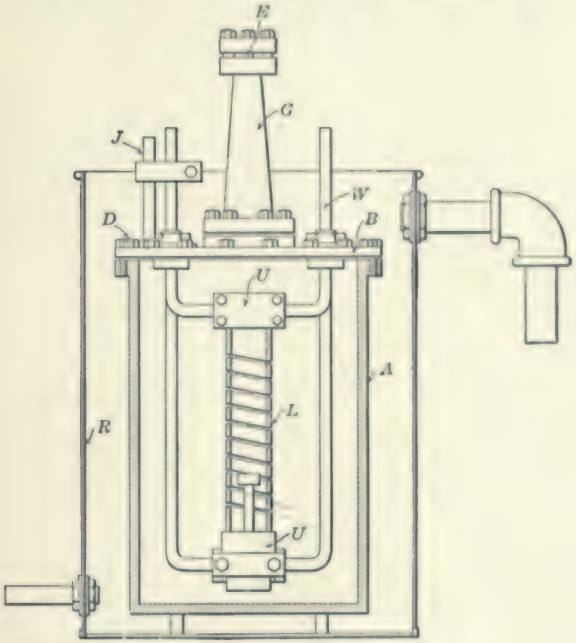


FIG. 133.

of 0.01 mm. in less than 15 min. The apparatus for collecting the carbon monoxide is shown in Fig. 134.

Procedure.—Care should be taken in preparing the sample as described on p. 348. Blank determinations should also be made to determine the quantity of carbon monoxide formed when no oxide is present; and in every analysis allowance must be made for the amount of carbon monoxide thus obtained.

[1] To be obtained from any large dealer in scientific apparatus

For the analysis itself, weigh 20 to 25 g. of the metal into a small graphite crucible and add 4 or 5 g. of powdered graphite. Place the crucible on the support in the furnace and bolt down the cover of the latter. By means of the vacuum pump, thoroughly exhaust the furnace, then turn on the cooling water and heat the furnace to about 500–600° with the pump still running. This is necessary to withdraw the oxygen absorbed by the heater and crucible. As carbon does not begin to reduce oxides below 900° there is no danger in heating the crucible up to 500°. After heating 15 min. at this temperature, allow the crucible

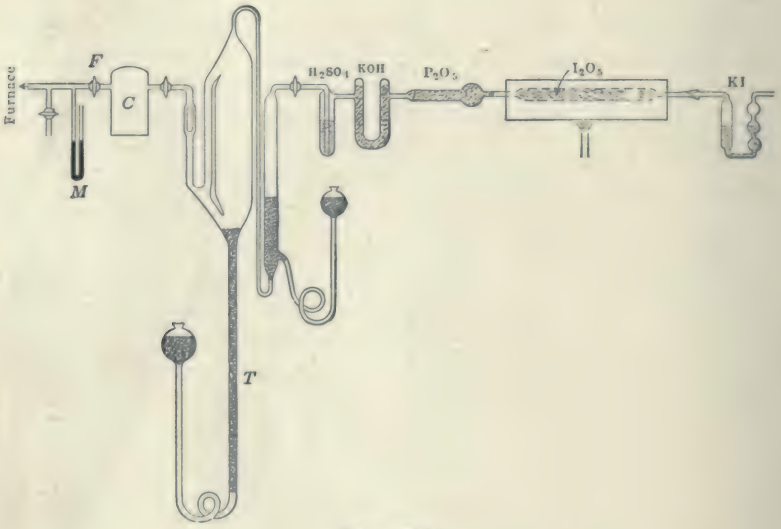


FIG. 134.

to cool, which it does very rapidly. Introduce nitrogen, that has been dried over sulfuric acid and phosphorus pentoxide, into the cold furnace until about half an atmosphere pressure is obtained. Again evacuate the furnace and heat gently as before. Only by such treatment is it possible to reduce the oxygen left in the tube to a reasonably small value.

Now turn off the stopcock leading to the pump and apply seventy volts to the electrodes, which causes a current of about 200 amperes to flow through the heater. A high temperature is obtained very quickly and the metal usually melts within 3 or 4

min. Just as the metal melts violent ebullition often occurs. To stop this open the circuit for a short time and allow the charge to cool somewhat. When the metal is quiet continue the heating for 20 min. Then cool the furnace thoroughly and finally fill the furnace to atmospheric pressure with nitrogen that has been dried over sulfuric acid and phosphorus pentoxide.

The gas now in the furnace is analyzed for carbon monoxide in the following manner:

Exhaust the vessel C, Fig. 134, by means of the Toepler pump, T, and connect it with the furnace as indicated in the drawing. Open the stopcock at the furnace and note, by means of the differential gage M, the difference between the atmospheric pressure and the pressure within the furnace. Open the stopcock F and fill C and the pump T with gas from the furnace. A decrease in pressure corresponding to the volume of gas withdrawn from the furnace is shown by the gage M. In this way it is easy to compute, without errors due to temperature variation, what fraction of the original volume of gas in the furnace is used for the analysis.

Slowly force the gas, through the purifying train of concentrated sulfuric acid, solid caustic potash and solid phosphorus pentoxide, into the tube containing iodine pentoxide which is heated to 130°; here the carbon monoxide is oxidized to carbon dioxide and an equivalent quantity of iodine is liberated. The iodine is absorbed in a 10 per cent. solution of potassium iodide and finally titrated with $N/100$ sodium thiosulfate solution.

Computation.—If n cc. of hundredth-normal sodium thiosulfate solution are used in titrating the iodine absorbed in the analysis of a sample weighing s grams and n_1 represents the number of cc. of the same thiosulfate used in a blank experiment, then

$$N \frac{(n - n_1)\ 0.008}{s} = \text{per cent. O}$$

NOTES.—In all cases an appreciable quantity of iodine is obtained in a blank experiment. This is accounted for in three ways: first, a practically constant quantity of iodine is set free when air or nitrogen free from carbon monoxide is led over hot iodine pentoxide; second, there is always a little absorbed oxygen retained on the walls and in the heater of the furnace; third, a trace of moisture is left in the furnace and reacts with the hot carbon. By keeping the temperature of the iodine pentoxide at 130° the oxidation of the carbon monoxide is com-

plete and the decomposition of the iodine pentoxide is reduced to a minimum. By carefully carrying out the analysis as outlined above, the weight of oxygen corresponding to a blank determination is about 12 mg.

Instead of using the Toepler pump, it is much more simple to use a mercury aspirator, replacing the reservoir *C* (Fig. 134) by a liter bottle which may be filled with mercury. It is then easy to withdraw a known fraction of the furnace contents and to force it through the iodine pentoxide tube.

Although the results obtained by the method are not as accurate as might be desired, and although the method requires a complicated apparatus and careful manipulation, it is nevertheless of value for determining the presence of oxides which are not indicated by the Ledebur method and serves to explain the discrepancies often noted between the oxygen content as determined by that method and the physical and chemical properties of the materials.

TEST ANALYSES

1. OXYGEN FROM FERRIC OXIDE, ALUMINA AND SILICA

To determine the accuracy with which the oxygen of a sample of iron or steel will be converted to carbon monoxide, a number of analyses were made using an iron of very low oxygen content, and adding known quantities of the various oxides in the pure form. In addition to iron oxide, only the very refractory oxides of aluminium and silicon were used; other more easily reducible oxides such as manganese and copper can introduce no difficulties. The weighed amount of pure oxide together with a known weight of iron was placed in the graphite crucible, covered with powdered graphite and heated as described. The following results were obtained:

	Weight of oxide	Oxygen calculated	Oxygen found
Ferric oxide	0.5650	0.1695	0.1700
Ferric oxide	0.6525	0.1960	0.1940
Ferric oxide	0.8400	0.2520	0.2440
Ferric oxide	0.1516	0.0455	0.0480
Alumina	0.4925	0.2310	0.2040
Alumina	0.1860	0.0875	0.0810
Alumina	0.3065	0.1440	0.1260
Silica	0.0673	0.0360	0.0342
Silica	0.0320	0.0181	0.0171

2. COMPARATIVE RESULTS BY THE LEDEBUR AND WALKER-PATRICK METHODS

Sample No. 1 was a special heat of open-hearth steel to which iron ore and an excess of manganese were added in the ladle. The finished steel gave evidence of having a high oxygen content. No. 2. was a high-grade, open-hearth steel. No. 3 was also an open-hearth steel and No. 4 was the same as No. 3 but from an ingot to which ore was added. Nos. 7 and 8 were samples of open-hearth steel and Nos. 9 and 10 were open-hearth iron. Nos. 11*a* and 11*b* were duplicate analyses of an ingot iron of early manufacture and Nos. 12*a* and 12*b* were duplicate analyses of ingot iron of later make.

No.	Per cent. C	Per cent Mn	Per cent. S	Per cent. P	Per cent Si	Per cent Cu	Per cent O, Ledebur	Per cent. O, Walker-Patrick
1	0.19	0.92	0.052	0.123	.....	.....	0.006	0.29
2	.....	.....	.....	.....	.....	.....	0.000	0.09
3	0.17	0.65	0.097	0.064	0.017	.....	.....	0.11
4	0.12	0.17	0.065	0.088	0.015	.....	.....	0.33
5	0.09	0.18	0.061	0.087	0.019	.....	.....	0.31
6	0.14	0.24	0.070	0.092	0.009	.....	.....	0.065
7	0.09	0.33	0.065	0.068	0.006	0.17	0.009	0.021
8	0.08	0.33	0.036	0.070	0.005	0.22	0.010	0.039
9	0.01	0.03	0.050	0.007	0.003	0.20	0.037	0.056
10	0.01	0.04	0.015	0.008	0.004	0.19	0.052	0.064
11*a*	0.01	trace	0.015	0.002	.....	.....	0.069	0.23
11*b*	0.01	trace	0.015	0.002	.....	.....	0.076	0.21
12*a*	0.02	0.03	0.029	0.004	0.0014	0.043	.....	0.10
12*b*	0.02	0.03	0.029	0.004	0.0014	0.043	.....	0.11

CHAPTER XVIII

NITROGEN

For many years nitrogen was believed to play an important part in the manufacture of steel. This view, however, has been discredited and the determination of nitrogen is one that is seldom included in the chemical examination of a sample of steel. Yet there is considerable evidence in the literature that the small quantities of nitrogen present in steel, rarely much more than 0.01 per cent., may have considerable influence upon the value of the product. As a rule, nitrogen produces brittleness, but whether this effect is produced by the element alone or only in conjunction with sulfur and phosphorus is not definitely settled. Stromeyer has claimed that nitrogen has 10 times more effect than phosphorus in raising the tenacity of steel, and states that in a good specimen of steel the percentage of phosphorus increased by 5 times the percentage of nitrogen should not exceed 0.080 per cent. Nitrogen is probably present in steel either as Fe_5N_2 or as Fe_4N_2.

1. DETERMINATION OF NITROGEN IN STEEL

Method of A. H. Allen.[1]

Principle.—When steel is dissolved in sulfuric or hydrochloric acid, all the combined nitrogen is obtained in the form of ammonium salt. If the solution is boiled with an excess of sodium hydroxide, ammonia is distilled off and can be determined by the Nessler test or by absorption in a measured volume of standard acid and titrating the excess of the latter with standard alkali. The quantity of nitrogen present is so small, however, that it requires a large sample of steel, 10 g. at least, to give enough ammonia to determine accurately by the latter method.

[1] First proposed by A. H. Allen (J. Iron and Steel Institute, **1879,** 480; **1880,** 181) and modified by J. W. Langley (*cf.* Blair's *Chemical Analysis of Iron and Steel*).

Reagents Required. *Distilled Water Free from Ammonia.*—Add a little potassium permanganate and some sodium carbonate to ordinary distilled water and redistil, rejecting the first fourth and last sixth of the distillate.

Standard Ammonium Chloride Solution.—Dissolve 0.0382 g. of pure ammonium chloride in 1 liter of water free from ammonia. One cubic centimeter of this solution is equivalent to 0.01 mg. of nitrogen.

Six-normal Hydrochloric Acid.—Half fill a liter flask with concentrated hydrochloric acid. Through a two-holed rubber stopper, which fits the neck of the flask, insert a dropping funnel and a gas delivery tube connecting the flask with a second flask containing pure water, free from ammonia. Pour some pure, concentrated, sulfuric acid, free from nitrous acid, into the dropping funnel and allow this to flow slowly into the hydrochloric acid, heating the contents of the flask as required. Distil the hydrochloric acid into the pure water until the specific gravity of the acid solution thus formed is about 1.1.

Sodium Hydroxide Solution.—Dissolve 300 g. of pure caustic soda in 500 cc. of water and digest it 24 hr. with a copper-zinc couple. To make the couple, cover about 25 g. of thin sheet zinc with a fairly concentrated copper sulfate solution; after about 10 min. pour off the solution and wash the residue of copper and zinc with cold, distilled water.

Nessler's Reagent.—Dissolve 61.75 g. of pure potassium iodide in 250 cc. of distilled water and add a cold, saturated solution of mercuric chloride, prepared by obtaining a hot, saturated solution and allowing the excess of the salt to crystallize out on cooling. Add the mercuric chloride solution very carefully, stopping when a slight permanent, red precipitate of mercuric iodide, HgI_2, is formed. Dissolve this by adding 0.75 g. of powdered potassium iodide and then add 150 g. of potassium hydroxide dissolved in 250 cc. of water. Make up to a liter and allow it to settle over night.

Carefully siphon off the clear solution into a clean bottle and keep it in a dark place. This solution should give the required color within 5 min. Nessler solution contains the complex salt $K_2[HgI_4]$. The alkaline solution reacts with ammonia, forming a brown precipitate, or a coloration varying with the quantity of

ammonia present; the reaction is expressed by the following equation:

$$2K_2[HgI_4] + 3KOH + NH_4OH = O\begin{matrix}Hg\\ \diagup\diagdown\\ Hg\end{matrix}NH_2.I + 3H_2O + 7KI$$

Procedure.—Place 30 cc. of the sodium hydroxide solution in the 500-cc. Erlenmeyer flask, *K*, Fig. 135, add 500 cc. of water and distil until a 50-cc. portion of the distillate, when treated with 1 cc. of Nessler reagent, will give less color than is obtained with

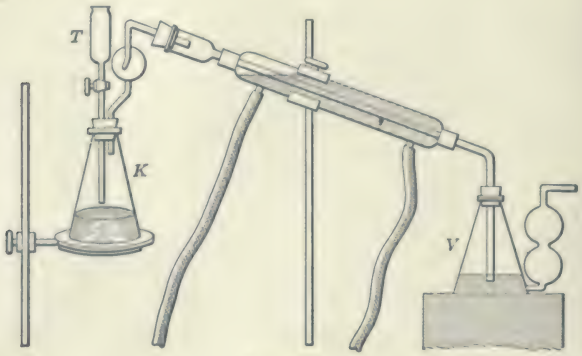


FIG. 135.

1 cc. of the standard ammonium chloride solution, diluted to 50 cc. with water free from ammonia, and similarly treated with Nessler reagent.

Meanwhile dissolve 3 g. of carefully washed steel turnings in 30 cc. of the pure, six-normal hydrochloric acid, heating if necessary. Transfer the solution to the bulb of the dropping funnel, *T*, and, when the solution in the flask is boiled free from ammonia, slowly add the ferrous chloride solution. Rotate the contents of the flask to make sure that a good mixture is obtained and then carefully continue the boiling. When about 50 cc. of distillate is obtained, transfer it to a Nessler tube, which is merely a long, cylindrical tube of uniform bore, mix it with 1 cc. of Nessler reagent and allow to stand 5 min. Compare the color with that obtained with 1, 2, 3, etc., cc. portions of standard ammonium chloride solution, each treated with 1 cc. of Nessler reagent,

diluted to 50 cc. with best water and allowed to stand 5 min. Hold the tubes side by side in a slightly inclined position and look down upon them with a background of white paper. The standards should be prepared at the same time the test is being made. Make a note of the number of cc. of ammonium chloride solution required to give the same shade as that of the Nesslerized distillate. Continue to collect portions of the distillate, and match them with the standards, until finally a 50-cc. portion is obtained which gives a distinctly paler color than that obtained with 1 cc. of the standard.

Computation.—If n represents the sum of the number of cc. of standard ammonium chloride solution required to match the various portions of the Nesslerized distillate, in the analysis of a sample of steel weighing s g., then

$$\text{per cent. N} = \frac{0.001\ n}{s}$$

2. MODIFICATION OF L. E. BARTON[1]

Dissolve 5 g. of the steel in 40 cc. of ammonia-free hydrochloric acid and add the solution to the distilling flask exactly as in the above directions. Catch the distillate in a graduated flask and distil until 150 cc. of distillate are obtained; this will contain all of the nitrogen, as experience has shown.

Then add 25 cc. of the standard ammonium chloride solution to the contents of the flask and distil into another graduated flask until 150 cc. of distillate are obtained, which will also contain all of the nitrogen in the standard. To this add 6 cc. of Nessler reagent. Since the standard solution contains 0.01 mg. per cc., the standard distillate will now contain $\frac{25 \times 0.01}{156} = 0.0016$ mg. per cc. A single standard distillate will serve for the determination of nitrogen in several samples of steel if the comparisons are being made at the same time.

For the color comparison, place 30 cc. of the distillate from the solution of the steel (= 1 g. of metal) into one of a pair of Nessler tubes, add 1 cc. of Nessler reagent and allow the color to develop by letting the solution stand 5 min. Into the other

[1] J. Ind. Eng. Chem., **6**, 1012 (1914).

Nessler tube run in the standard distillate until the colors in the two Nessler tubes match, making the final comparison after bringing the solutions to the same volume by the addition of distilled water free from ammonia to one or the other of the tubes. Then the number of cc. of standard distillate used multiplied by 0.0016 gives the percentage of nitrogen in the steel.

The results in duplicate determinations by this method do not usually differ by more than 0.0005 per cent. nitrogen. The average nitrogen content of steel is about 0.004 per cent.

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Caesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulfur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum[1]	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	3.99	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

[1] Also called Beryllium, Be.

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